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BUILDING 49 STUDY

ASSESSMENT OF SOIL CONTAMINATION  
AND POTENTIAL CONTAMINANT MIGRATION

Prepared for TRW, INC.  
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Modified  
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## 1. INTRODUCTION

TRW Inc., retained Engineering-Science (ES) to determine the extent of previously unsuspected discharges from the Building 49 Torpedo Test facilities. Soil sampling in support of this began in October 1985 and continued through several stages through October of 1986. TRW also authorized a coordinated assessment of potential effects of those discharges on surface water and ground water. This report summarizes the results of those studies and ES' recommendations for remedial action.

### 1.1 BACKGROUND AND SITE CONDITIONS

TRW Inc., conducted torpedo engine testing in Building 49, in the southeastern portion of its former TAPCO complex in Euclid, Ohio. Wastewater resulting from test firing activities has been discharged through a 1,000 gallon underground steel separator tank, which was designed to remove and collect liquid residues of the torpedo fuel. The overflow from this tank discharged through an underground pipeline onto the soil in an undeveloped area about 100 feet southeast from the building. Modifications of the facilities in Building 49 have been installed, and further discharges of the fuel residue have been eliminated. Torpedo testing activities are being transferred to new facilities elsewhere on the TAPCO complex.

The affected area is shown in relation to Building 49 in Figure 1 (See also appended Drawings 1 & 2). The now-discontinued discharges were released from an underground pipe in a flat undeveloped area to the southeast of Building 49, bounded on its north by the torpedo test area fence and by woods on its other sides. The former discharge area has typical swamp vegetation. Field activities have shown that the poor drainage is attributable to a layer of low permeability clay ( $10^{-6}$  to  $10^{-8}$  cm/sec) which was found typically about 3 feet below the surface.

Run-on from the soil mound (explosion barrier for the torpedo testing) flows southeastward across the former discharge zone and drains southward through the runoff stream, as indicated on Drawing 2. Additional run-on from wooded areas to the north and east drains through the area immediately

to the southeast of the former discharge zone, and into the same runoff stream.

During the summer months, there was additional run-on due to daytime flows of 12-15 gpm city water through the Building 49 air conditioning unit, which discharged by pipeline in a wooded area to the northeast of the building. (Analysis of the air conditioner effluent showed no detectable concentrations of cyanides.)

The runoff stream flows southward through a wooded strip and emerges into a cleared area adjoining the roadway. A sorbent boom has been placed across the stream at the edge of the woods. From there, the stream discharges through a corrugated steel culvert (which is half filled with sediments), enters a drainage swale paralleling the roadway, then crosses under the roadway through a culvert, and discharges directly into a catch basin for the storm sewers. The 30-inch storm sewer serving the eastern part of the property proceeds westward about 300 ft to join other storm drains, and then along a northwesterly alignment to discharge into a culvert at the property line.

## 1.2 NATURE OF THE CHEMICALS DISCHARGED

The torpedo fuel, Otto Fuel II, is a liquid mixture consisting of about 76 percent propylene glycol dinitrate (PGDN), 22.5 percent di n-butyl sebacate and 1.5 percent 2-nitro diphenyl amine, which is stable at ambient pressures and temperatures. The fuel is heavier than water (specific gravity = 1.23) and is essentially immiscible with water. It is not volatile; the vapor pressure is 0.09 mm of mercury at 77°F.

Physical exposure by absorption through the skin or by ingestion is known to cause severe headaches, but definitive toxicity data are not available. Otto Fuel is considered hazardous, subject to liquid hazard classification Group 1 (combustible, but low fire hazard, with flash point 265°F) and compatibility Group G (not to be stored near other hazardous materials). [1] However, it is not flammable according to U.S. Department of Transportation or RCRA (Resource Conservation and Recovery Act) criteria since the flash point exceeds 140°F.

Wastewater discharges to the separator were intermittent, mainly in 200 to 300 gallon batches during and shortly after a torpedo test firing. Normally, the separator tank removed the liquid fuel residue effectively.

It was not previously suspected that turbulence at high flow rates through the tank entrained droplets of fuel residue into the former discharge pipe. This was confirmed during actual test firings in July 1985.

Exhaust gases from torpedo test firings were vented to the atmosphere through 4-inch diameter stacks, about 20 feet above ground level. The exhaust gases typically contained low concentrations of hydrogen cyanide and ammonia resulting from incomplete combustion of Otto Fuel. Any condensate droplets in the exhaust gas would have discharged into drainage piping leading to the separator tank for waste water discharges. Cyanides were present in the discharges from the separator tank as a result of this. Analysis of grab samples taken at the former discharge pipe, authorized by TRW prior to this study, showed concentrations of 3 to 26 mg/L of total cyanide.

### 1.3 SCOPE OF STUDIES

The Building 49 study consisted of coordinated soil sampling, surface water monitoring and ground water monitoring activities. The methods of investigation and the principal findings for these phases of the study are reported in Sections 3,4 and 5, respectively. The methods for chemical analysis of samples from all phases of the study are presented in Section 2. The results are reviewed in Section 6, and recommendations are presented for closure of the discharge area and the Building 49 site.

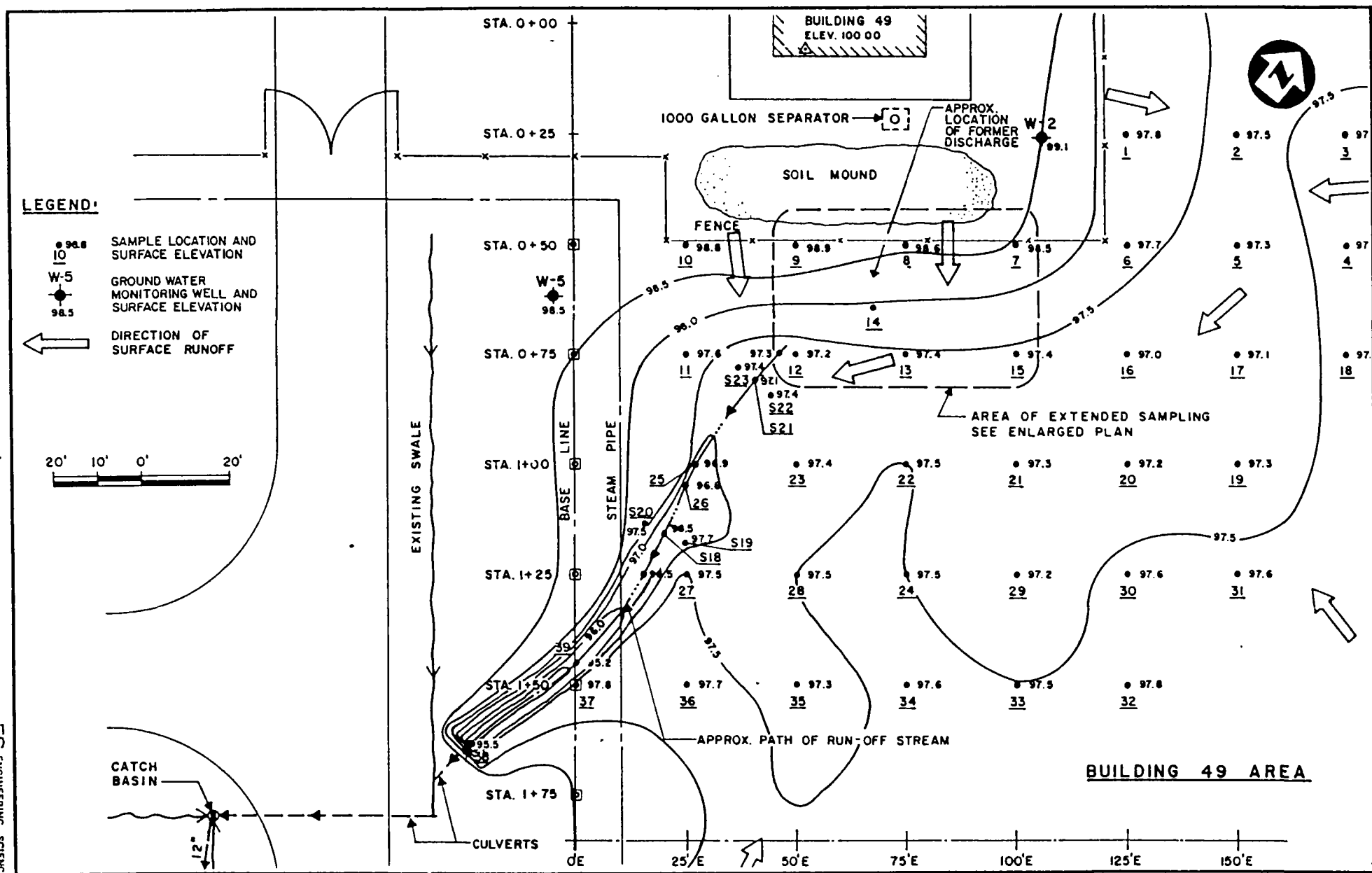


FIGURE 1

## 2. METHODS OF CHEMICAL ANALYSIS

All samples in this study were transported to Wadsworth/Alert Laboratories, Canton, Ohio for analysis. Their reports are appended. Wadsworth has been designated by the U.S. Environmental Protection Agency (USEPA) as a Contract Laboratory Procedures facility for analysis of soil samples. Wadsworth has also been certified by the Ohio EPA for analysis of water and wastewater.

### 2.1 OTTO FUEL

The analysis for propylene glycol dinitrate (PGDN), the principal ingredient of Otto Fuel II, consisted of an acetone extraction followed by gas-liquid chromatography using a flame ionization detector. Otto Fuel II, nominally containing 76 percent PGDN, was used as a standard for calibration.

The detection limit for PGDN in a soil sample was 300 mg/kg for the initial sampling. This was improved to 25 mg/kg for the later soil samples and 125 mg/kg in a sample of suspect vegetation. The detection limit for PGDN in sediment samples varied from 60 to 80 ug/L (of unfiltered slurry), depending on sample size.

TRW authorized development of this analytical technique by Wadsworth, in conjunction with this study. The only other known analytical method is a wet-chemical technique [1], which has much higher detection limits.

### 2.2 CYANIDE

The cyanide analysis used the "total" cyanide technique (EPA Method 9010: acidification, volatilization and alkaline absorption), which is the standard for soil, sediment and solid waste samples. [2] The detection limit was 0.25 mg/kg of cyanide for soil samples and 0.005 mg/L for water samples. This method is quantitative for all forms of cyanide except the essentially non-toxic complexes of iron and cyanide.

### 2.3 SAMPLE PRESERVATION AND PREPARATION

Soil core samples were taken in carbon steel pipes, sealed at the site, and transported to the laboratory by Engineering-Science (ES). Chain-of-custody documentation was provided, although not formally required for the study.



Upon arrival at the laboratory, selected cores were cut to provide samples representing desired depth intervals. The soil core samples that were not analyzed initially were retained at the laboratory and stored in a cold room for possible later analysis, pending the results for other related samples.

### 3. DIRECTED SOIL SAMPLING PROGRAM

Soils in and near the former discharge area was sampled on four occasions between October 1985 and October 1986. The sample locations and analytical data are summarized in Table 1 and Figures 2 through 4 (Also see appended Drawings 3 through 5). The principal findings are as follows:

- o An irregularly shaped area surrounding the former discharge pipe has Otto Fuel residue present at the surface (in the top 1 ft) at concentrations of 150 to 4,900 mg/kg of PGDN and Total Cyanide at concentrations of 5 to 50 mg/kg.
- o PGDN was found at only one location below the top 1 ft., i.e., at the former discharge pipe outlet. Here, 80 mg/kg of PGDN was found in a composite sample from a 2 ft depth to the bottom of the core.
- o At specific isolated locations in the runoff stream, 30 to 70 feet from the former discharge pipe, soil in the top 1 ft was found containing 89 to 240 mg/kg of PGDN and/or 5 to 20 mg/kg of Total Cyanide (See Figure 4 and appended Drawing 3).
- o Cyanide was also found in the top 1 ft of soil at detectable, but low concentrations, typically 0.5 to 4 mg/kg, along a narrow belt of adjoining sampling stations, encircling Building 49 at distances of 75 to 300 ft. A clear zone, with cyanides below the detection limits, lies between Building 49 and this belt.
- o Cyanide was detected below the top 1 ft of soil at or near the same sample locations (that had detectable cyanides in the top 1 ft), generally at lower concentrations than at the surface. However, three isolated sample locations along the belt of stations to the south and east of Building 49 had their highest cyanide concentrations (of 1.4 to 4 mg/kg) at the bottom.

It is believed that the Otto Fuel residue droplets settled rapidly after being released in the area near the former discharge pipe outlet and were absorbed by surface soil particles. Occasionally, isolated particles of soil were eroded, which mobilized small quantities of PGDN. However, cyanides in the torpedo test wastewater discharges, being soluble, spread over a larger area. Cyanides would be mobilized either by erosion or by leaching.

Cyanides in the belt to the south and east of Building 49 are attributed to deposition by downwash of exhaust gases vented during the torpedo testing.

A narrative of the soil sampling methods and the tentative findings at each stage follows.

### 3.1 OCTOBER 1985 SOIL SAMPLING

The initial sampling had as its objectives to confirm that discharges of torpedo fuel residue and cyanides had occurred, and to indicate whether either or both of these chemicals had spread away from the former discharge pipe. This sampling utilized hand augers and was limited to the top three feet. Some of the sample locations were ponded over at the time.

At the former discharge pipe, PGDN concentrations of 800 to 1,300 mg/kg were found, along with Total Cyanide at 3 to 1 mg/kg. Both chemicals were present in the samples representing the top 1 ft, the second 1 ft and the third 1 ft. This apparent vertical migration may have been due to movement of material from the surface into the lower samples, which could not have been prevented under the field conditions.

Cyanide was found at a location near the runoff stream, at concentrations of 11 mg/kg in the top 1 ft and at 1 to 2 mg/kg in the next 2 ft below that. Cyanide also was detected at 0.9 mg/kg in the top 1 ft at a location to the southeast of the former discharge pipe.

Samples also were collected at this time at two suspected spill locations at the northeast corner of the torpedo test complex. PGDN was not detected in either of these samples. However, cyanide was present at concentrations of 4 to 6 mg/kg.

### 3.2 MAY AND AUGUST 1986 SOIL SAMPLINGS

TRW authorized additional soil sampling and a survey of the area to define both the vertical and the lateral extent of soil contamination. In order to ensure personnel safety (See Appendix A, ES Health and Safety Report for this project), the sampling used a rig which could be operated some distance away from the former discharge area, on dry ground. The rig locations are noted on appended Drawing 1.

The sampling rig was a modified sheet piling driver, attached to a crane. Sample cores were obtained by driving a steam cleaned 10 foot length of 3-inch carbon steel pipe to refusal (typically 4 to 7 feet), withdrawing the pipe and sealing the ends. This effectively eliminated cross-contamination (between samples representing different depths). The core hole was refilled with powdered bentonite.

During the week of 31 March - 4 April 1986, 39 locations southeast of Building 49 were sampled, most of them within the ponded area, on the 25 ft center grid shown on Figure 1 and the appended drawings. Four of these samples (25, 26, 38 and 39) were from points in the runoff stream.

Concentrations of 1,600 mg/kg PGDN and 5.7 mg/kg CN were found at the surface near the former discharge pipe (Sample 14), confirming the previous results. However, neither chemical was detected in the bottom 1 ft of that sample core. PGDN was also found at a concentration of 89 mg/kg in the top 1 ft of sediments, at a pool in the runoff stream (Sample 26). Cyanide was detected at these points and at several other locations, either at the surface or at the bottom of the core.

During the 4-7 August 1986 period, 29 additional points (S-1 through S-29) were sampled, most of these being on a 5 ft center grid superimposed on the coarser grid in the vicinity of the former discharge pipe (See Figure 2 and the inset on appended Drawings 2 through 7). Two points in the runoff stream and four locations on the adjoining banks (S-18 through S-23) were included in this sampling. Selected cores were analyzed sequentially, starting with the top 1 ft section and in some cases continuing with the next lower 1 ft section and a composite of the remaining material below 2 ft.

PGDN and Cyanide were found in the top 1 ft at several sample locations near the former discharge pipe. PGDN concentrations there ranged from 150 to 3,900 mg/kg, and Cyanide ranged from 5 to 50 mg/kg. PGDN was

detected below the top 1 ft in only one of the sample cores (S-29), at the same location that had the highest surface PGDN concentration. Cyanide was detected below the top 1 ft at the locations near the former discharge pipe, at concentrations of about 1 mg/kg.

### 3.3 OCTOBER 1986 SOIL SAMPLING

Another nine soil core samples (T-3 through T-11) were collected on 16 October 1986, at locations on an extension of the 5 ft center grid eastward from the former discharge pipe (See Figure 2 and the inset on appended Drawings 2 through 7). These additional soil cores were collected by a modified Shelby Tube method, using 3 ft lengths of 2-inch black iron pipe threaded on one end. The pipe was driven into the ground with a sledge to a depth of 2-3 feet and manually withdrawn. The pipe ends were closed with plastic immediately after collection of the sample. The pipe was cleaned with detergent solution and pressurized water spray before sample collection.

Samples were analyzed from the four points closest to the August samples, abouts 20 ft to the east of the former discharge. PGDN was not detected in any of these cores. The cyanide concentrations were 5 to 15 mg/kg in the top 1 ft of soil, but less than 1 mg/kg for depths of 1 ft-2ft.

### 3.4 SEPTEMBER 1986 WELL INSTALLATION

Five wells were installed during the week of 5 to 8 September 1986, for the ground water monitoring activities discussed in Section 5. The wells were located 25 to 75 feet beyond the area of soil sampling of the former discharge area (See appended Drawing 1). During the well installation, the augers were cleaned between holes to eliminate cross-contamination. Undisturbed Shelby-tube samples of the unconsolidated sediments (W-1 through W-5) were obtained at shallow intervals. Generally, one tube was obtained for the 1 ft - 3 ft interval and another tube for the 3 ft - 5 ft interval.

All of the Shelby-tube samples were analyzed for Total Cyanide. It was found at the three northerly well locations, at concentrations of 1 to 2 mg/kg, at the 1 ft - 3 ft level. It was not detected below that depth. Sediment samples from Wells W-2 and W-3 were also analyzed for PGDN, based

on the field observation that the silty clays just above bedrock appeared to be stained dark gray to black; the PGDN concentrations were below the detection limit of 25 mg/kg in both of those samples.

### 3.5 JUNE 1987 SOIL SAMPLING

Additional Shelby-tube soil sampling and laboratory analysis for cyanides was undertaken, to further define the extent of soils containing cyanides and to determine characteristics of the soil in the vicinity of Building 49, for purposes of treatment and disposal.

The soil samples at the former discharge pipe (C-13 through C-15) averaged 543 mg/kg PGDN and 17 mg/kg cyanides, similar in those noted in previous samplings. Priority pollutant organics and PCBs were not present at detectable concentrations.

Additional characteristics were determined for possible treatment of soil excavated from the former discharge area by incineration (to be followed by ultimate disposal of the resultant ash by landfilling). The observed high flash point ( $>180^{\circ}\text{F}$ ), low net heating value ( $<1,000$  BTU/lb), high ash content (72 percent) and high solids content (73 percent) in discharge area samples were essentially the same as those of background soil samples taken further away from there.

The belt of detectable cyanides was found to continue on the north and west of Building 49, with concentrations of 0.5 to 2 mg/kg in the surface soils at distances up to 300 ft from the building (Sample Stations B-1 through B-4 and C-1 through C-12). However, the belt does not appear to extend into wooded land further to the east.

The soil mound south of Building 49 was also sampled and analyzed for cyanides. The concentration for a composite sample was below the detection limit of 0.25 mg/kg.

### 3.6 SPREADING OF PGDN AND CYANIDES FROM THE FORMER DISCHARGE AREA

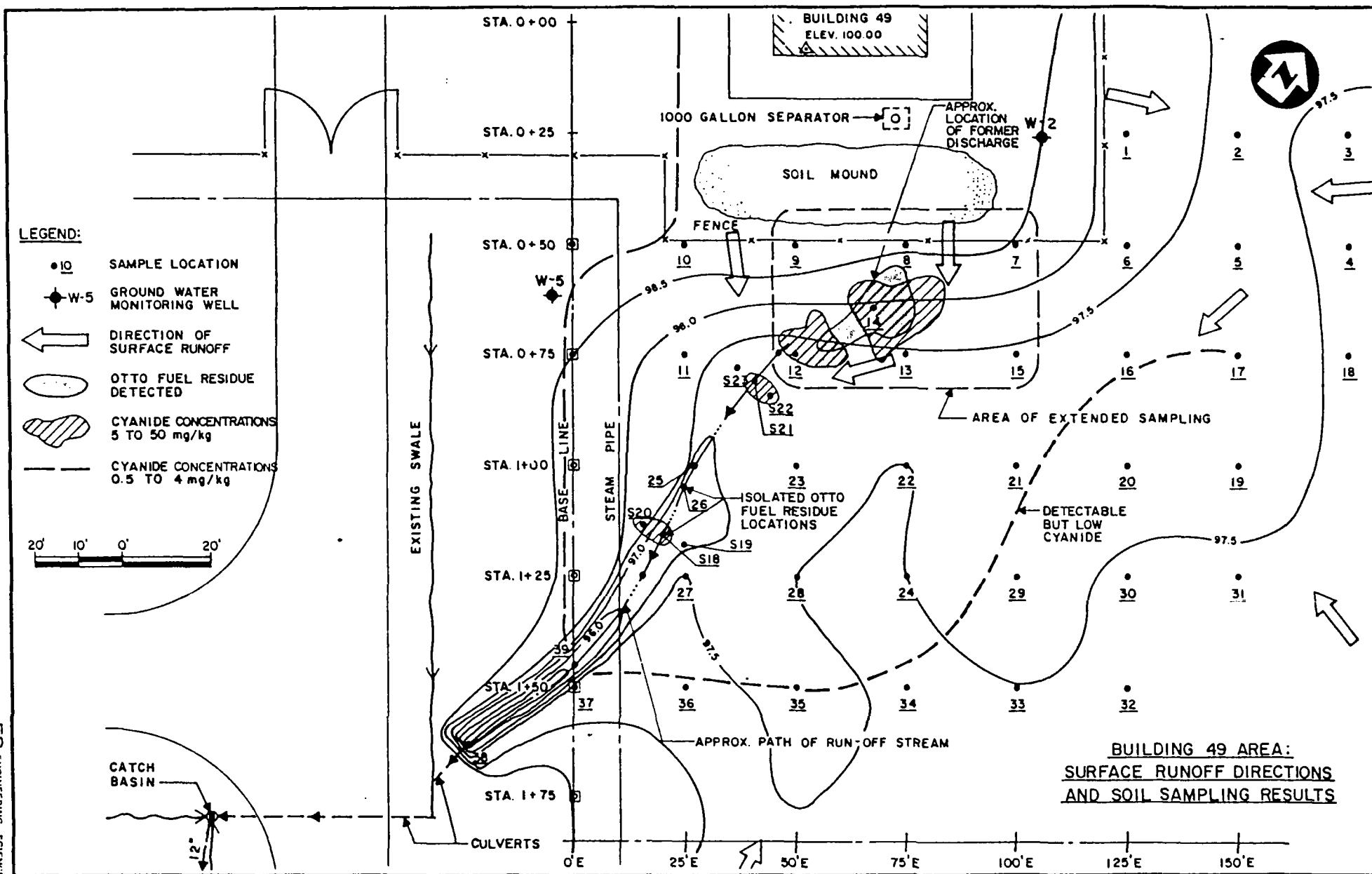
Figures 2 and 3 indicate the results of the soil sampling. The highest concentrations of Otto Fuel residue and cyanides are in an irregularly shaped area surrounding the former discharge pipe. Somewhat lower concentrations were found in the runoff stream, at specific isolated locations 30 to 70 feet away from there.

Detectable PGDN concentrations (solid lines in Figures 3) cover a portion of the area of highest concentrations, approximately on the path for drainage between the former discharge pipe and the runoff stream. It is believed that Otto Fuel residue droplets settled rapidly after discharge and were absorbed by surface soil particles. This essentially immobilized the water-immiscible fuel components, except for occasional isolated instances of erosion. Runoff from the soil mound to the northwest flowing directly over the discharge area could dislodge soil particles containing PGDN, carrying and depositing them into the runoff stream.

Detectable cyanide concentrations (dashed lines) near the former discharge pipe cover a larger area than PGDN. Soluble cyanides are spread over a larger area, having been mobilized either by erosion or by leaching. Cyanides also are subject to volatilization, chemical destruction and microbiological degradation, which may account for the bisection of the zones of high cyanide concentrations (5 to 50 mg/kg), at the former discharge area by a narrow belt of low cyanide concentrations.

Cyanide was also found at detectable, but low concentrations, typically about 1 mg/kg, along an encircling belt of adjoining sampling stations, 75 to 300 ft from Building 49. This is attributed to deposition of atmospheric cyanides by downwash of exhaust gas vented during the torpedo test firings. The cyanides at these locations would be subject to mobilization by leaching and to the degradation mechanisms noted above.

Subsurface cyanide concentrations generally decreased with depth below the surface and were found only at or adjoining locations with detectable surface cyanide concentrations. However, three isolated sample locations along the belt to the south and east of Building 49 had their highest cyanide concentrations (of 1.4 to 4 mg/kg) at the bottom of the soil core.





NOTE: PGDN 80 mg/kg 2' DEPTH  
TO BOTTOM OF CORE  
AT S29 PGDN BOT BELOW  
IFT. AT ALL OTHER  
LOCATIONS TESTED

SOIL MOUND



45' E 50' E 55' E 60' E 65' E 70' E 75' E 80' E 85' E 90' E 95' E 100' E

FENCE

STA. 0+50

STA. 0+55

STA. 0+60

STA. 0+65

STA. 0+70

STA. 0+75

**LEGEND:**

- ORIGINAL SAMPLING POINT
- EXTENDED SAMPLING POINT
- OTTO FUEL RESIDUE CONCENTRATIONS (AS mg/kg OF PGDN)
- - - CYANIDE CONCENTRATIONS

0' 5' 10'

**SOIL SAMPLING RESULTS**

**NEAR THE FORMER DISCHARGE PIPE**

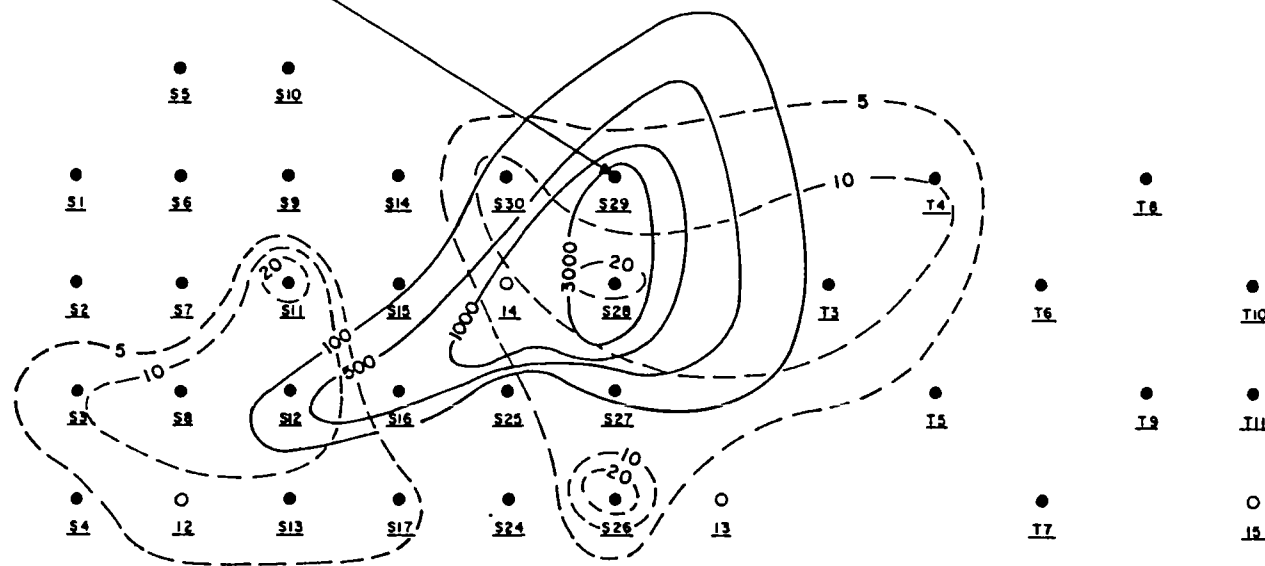


FIGURE. 4

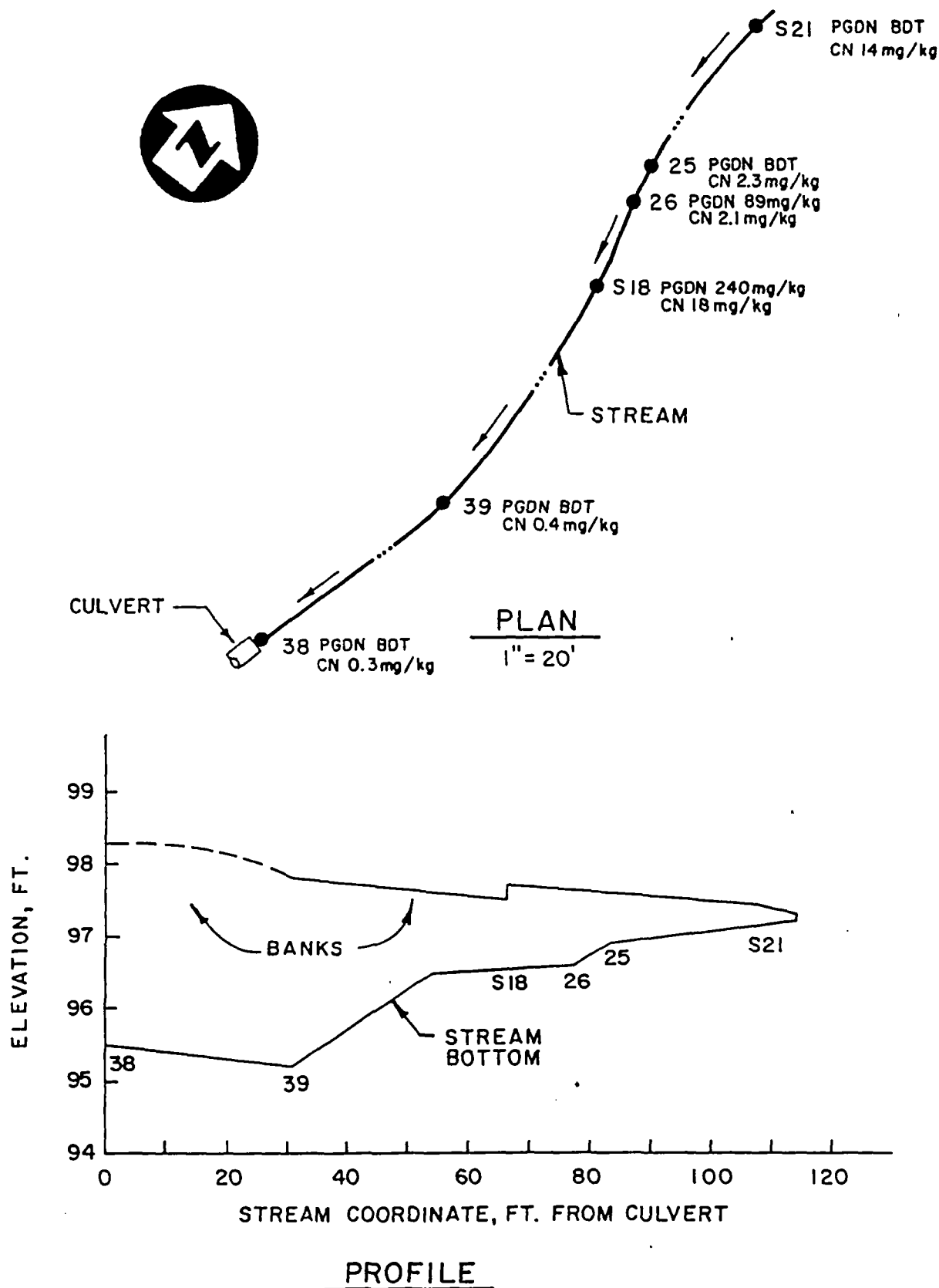


Table 1

## Summary of Building 49 Soil Sampling

Sample No.	Analytical Results (mg/kg)				Locations(ft)		Core Length (ft)	
	Top 1 ft		Bottom 1 ft		Surface Coordinates		as Driven	Compac -ted
	CN	PGDN	CN	PGDN	Elev.	South East		
1	BDT	BDT	BDT	BDT	97.8	25 125	5.7	4.8
2	BDT	BDT	BDT	BDT	97.5	25 150	5.3	4.4
3	BDT	BDT	BDT	BDT	97.6	25 175	4.9	5.0
4	BDT	BDT	BDT	BDT	97.7	50 175	4.5	3.8
5	BDT	BDT	BDT	BDT	97.3	50 150	4.7	4.1
6	BDT	BDT	BDT	BDT	97.7	50 125	5.3	5.2
7	BDT	BDT	BDT	BDT	98.5	50 100	6.3	4.7
8	BDT	BDT	BDT	BDT	98.6	50 75	5.9	4.0
9	BDT	BDT	BDT	BDT	98.9	50 50	6.4	4.8
10	1.2	BDT	BDT	BDT	98.8	50 25	5.7	3.8
11	0.8	BDT	BDT	BDT	97.6	75 25	4.9	4.5
12	7.4	BDT	BDT	BDT	97.2	75 50	5.3	4.6
13	0.9	BDT	BDT	BDT	97.4	75 75	4.9	3.9
14	5.7	1600	BDT	BDT	97.4	65 65	5.3	4.9
15	BDT	BDT	BDT	BDT	97.4	75 100	5.0	4.4
16	0.3	BDT	0.5	BDT	97.0	75 125	5.3	5.0
17	0.7	BDT	BDT	BDT	97.1	75 150	5.6	4.4
18	BDT	BDT	BDT	BDT	97.6	75 175	5.1	4.3
19	BDT	BDT	BDT	BDT	97.3	100 150	4.5	3.9
20	BDT	BDT	1.4	BDT	97.2	100 125	4.8	4.0
21	0.3	BDT	0.3	BDT	97.3	100 100	4.6	4.0
22	BDT	BDT	BDT	BDT	97.5	100 75	4.7	4.2
23	BDT	BDT	BDT	BDT	97.4	100 50	4.3	4.1
24	BDT	BDT	BDT	BDT	97.5	125 75	4.4	3.7
* 25	2.3	BDT	BDT	BDT	97.7	100 25	4.3	3.9
* 26	2.1	89	0.5	BDT	96.6	105 25	4.0	4.0
27	BDT	BDT	BDT	BDT	97.5	125 25	4.5	3.7
28	BDT	BDT	BDT	BDT	97.5	125 50	4.7	3.7
29	0.3	BDT	BDT	BDT	97.2	125 100	4.4	3.5
30	BDT	BDT	BDT	BDT	97.6	125 125	4.6	3.6
31	BDT	BDT	1.0	BDT	97.6	125 150	4.8	3.5
32	BDT	BDT	BDT	BDT	97.8	150 125	4.6	3.5
33	BDT	BDT	BDT	BDT	97.5	150 100	5.0	4.0
34	0.3	BDT	2.8	BDT	97.6	150 75	5.8	4.0
35	0.4	BDT	0.3	BDT	97.3	150 50	4.6	4.0
36	BDT	BDT	BDT	BDT	97.7	150 25	4.7	3.6
37	0.7	BDT	0.3	BDT	97.8	150 0	7.3	7.7
* 38	0.3	BDT	BDT	BDT	95.5	163 -25	4.8	4.6
* 39	0.4	BDT	3.9	BDT	95.2	145 0	5.6	4.8

\* = stream sampling point      -- = not analyzed

BDT = below detection limits: 0.25 mg/kg Total CN and 25 mg/kg PGDN  
Datum for elevations 100.0 ft = floor level in Building 49

Table 1 (continued)

## Summary of Building 49 Soil Sampling

Sample No.	Analytical Results (mg/kg)						Locations (ft)			Core Length (ft)	
	Top 1 ft		1 ft-2 ft		Below 2 ft		Surface Coordinates			as Driven	Compacted
	CN	PGDN	CN	PGDN	CN	PGDN	Elev.	South	East		
S-1	--	--	--	--	--	--	97.6	60	45	6.0	4.8
S-2	4.3	--	--	--	--	--	97.4	65	45	5.8	5.3
S-3	9.5	BDT	4.3	--	--	--	97.2	70	45	5.2	4.8
S-4	0.95	BDT	1.4	--	--	--	97.2	75	45	5.3	4.8
S-5	--	--	--	--	--	--	98.1	55	50	6.2	4.3
S-6	--	--	--	--	--	--	97.6	60	50	5.6	4.8
S-7	1.4	BDT	--	--	--	--	97.3	65	50	5.5	4.8
S-8	13	BDT	1.5	BDT	--	--	97.2	70	50	5.8	4.8
S-9	1.5	BDT	--	--	--	--	97.5	60	55	6.2	5.0
S-10	--	--	--	--	--	--	98.1	55	55	7.7	7.7
S-11	26	BDT	--	--	--	--	97.3	65	55	5.7	4.7
S-12	15	480	1.2	BDT	--	--	97.3	70	55	5.0	4.4
S-13	6.3	BDT	1.5	BDT	--	--	97.3	75	55	5.2	4.8
S-14	1.5	BDT	0.74	BDT	--	--	97.6	60	60	5.7	4.0
S-15	0.9	BDT	0.61	BDT	--	--	97.3	65	60	5.6	5.0
S-16	2.0	800	0.58	BDT	--	--	97.3	70	60	5.6	4.6
S-17	6.0	BDT	--	--	--	--	97.4	75	60	5.1	4.1
* S-18	18	240	1.0	BDT	--	--	96.5	116	20	4.2	4.2
S-19	--	--	--	--	--	--	97.7	118	24	n/a	n/a
S-20	6.1	BDT	BDT	BDT	--	--	97.5	114	16	5.8	6.5
* S-21	14	BDT	2.1	--	--	--	97.1	81	42	4.9	4.0
S-22	4.7	BDT	1.4	--	--	--	97.4	84	45	5.2	4.9
S-23	1.1	BDT	0.81	--	--	--	97.4	78	38	4.4	4.1
S-24	1.1	BDT	--	--	--	--	97.1	75	65	5.0	4.4
S-25	3.8	BDT	0.52	BDT	--	--	97.3	70	65	5.2	4.2
S-26	40	BDT	--	--	--	--	97.4	75	70	5.2	4.8
S-27	7.2	150	--	BDT	--	--	97.3	70	70	5.7	5.2
S-28	54	3600	1.4	BDT	1.5	BDT	97.5	65	70	5.6	4.8
S-29	5.5	4900	0.77	BDT	BDT	80	97.7	60	70	6.2	5.9
S-30	11	150	0.73	BDT	--	--	97.6	60	65	6.0	5.4
T-3	14	BDT	0.66	BDT	--	--	97.5	65	80	>2.0	
T-4	9.1	BDT	BDT	BDT	--	--	97.6	60	85	>1.5	
T-5	4.7	BDT	0.54	BDT	--	--	97.3	70	85	>2.0	
T-6	--	BDT	--	BDT	--	--	97.5	65	90	>2.0	
T-7	1.2	BDT	0.93	BDT	--	--	97.5	75	90	>2.0	
T-8	--	BDT	--	BDT	--	--	97.7	60	95	>1.5	
T-9	--	BDT	--	BDT	--	--	97.2	70	95	>2.0	
T-10	--	BDT	--	BDT	--	--	97.6	65	100	>2.0	
T-11	--	BDT	--	BDT	--	--	97.6	70	100	>2.0	
W-1	--	--	BDT	--	BDT	--	97.7	198	123	4.5	
W-2	--	--	2.0	BDT	BDT	BDT	99.1	25	106	5.5	
W-3	--	--	--	--	2.0	BDT	98.9	-63	-5	6.0	
W-4	--	--	BDT	--	BDT	--	98.3	212	19	5.5	
W-5	--	--	1.2	BDT	BDT	BDT	98.5	63	-5	6.5	

\* = stream sampling point      -- = not analyzed      n/a = core not recovered

BDT = below detection limits: 0.25 mg/kg Total CN and 25 mg/kg PGDN

Datum for elevations 100.0 ft = floor level in Building 49

Table 1 (cont'd)

## Summary of Building 49 Soil Sampling

Sample No.	Analytical Results (mg/kg)						Coordinates	
	Top 1 ft		1 ft- 2 ft		Below 2 ft		South	East
	CN	PGDN	CN	PGDN	CN	PGDN		
B -1	BDT	--					-287	-139
B -2	1.9	--					-282	139
B -3	1.0	--					225	-10
B -4	BDT	--					229	181
C -1	1.5	--					-108	91
C -2	2.2	--					-245	100
C -3	2.4	--					-157	7
C -4	1.5	--					-132	-30
C -5	0.5	--					-18	-72
C -6	0.5	--					59	-105
C -7	BDT	--					-75	224
C -8	BDT	--					-126	200
C -9	BDT	--					0	237
C-10	BDT	--					-25	175
C-11	BDT	--					138	112
C-12	BDT	--					75	137
C-13	11	BDT					61	78
C-14	16	1300					70	56
C-15	23	330					66	66

-- = not analyzed      Series B and C sampled only for top 1 ft.

BDT = below detection limits: 0.25 mg/kg Total CN and 25 mg/kg PGDN

#### 4. SURFACE WATER STUDY

In August 1986, TRW authorized a study to assess potential migration of PGDN and Cyanide from the original affected area near Building 49 through surface water and ground water. This section deals with the assessment for surface water movement.

Table 2 summarizes the surface water monitoring and associated chemical analysis data. The principal findings with respect to surface water are as follows:

- o Isolated and occasional soil particles containing Otto Fuel residue (mainly PGDN) have migrated out of the original affected area through the runoff stream and have entered the storm sewer system.
- o The runoff stream also contains detectable, but low concentrations of Cyanide, typically not exceeding 1 mg/L.

Details follow on the studies that led to these findings.

##### 4.1 SURFACE WATER RUNOFF MONITORING

The runoff stream flow exiting from the formerly swampy area south of Building 49 was monitored twice during September 1986, first during a low flow period after extended dry weather on 16 September, and a second time on 24 September, several hours after a moderate rain. The flow at the first culvert was measured with a portable weir on both occasions, and multiple grab samples were collected and field composited for Total Cyanide analysis. (The PGDN concentrations would have been below the detection limit of 25 mg/kg, since it is not miscible with water.)

The dry weather monitoring showed total flow of the runoff stream less than 3 gallons/day, but with a Total Cyanide concentration of 1.2 mg/L. After a moderate rainfall, the runoff stream flow was measured at about 1,760 gal/day, with a Total Cyanide concentration of 0.24 mg/L.

The Building 49 air conditioning discharge flow was also monitored on the same dates. At the entry to the pipeline that discharges the air conditioning effluent into the wooded area to the east of the building, the observed flows ranged from 13 to 15 gal/min (17,000 to 21,000 gal/day).

Grab samples from this stream did not contain Cyanides at detectable concentrations.

#### 4.2 OTTO FUEL RESIDUE MIGRATION IN THE RUNOFF STREAM

The Surface Water Study provided additional evidence confirming that the occasional erosion of isolated soil particles containing Otto Fuel residue had carried them through the runoff stream.

TRW maintenance crews cleaned the runoff stream channel during the late fall of 1985. Leaves and debris removed from the stream in that operation were placed in the wooded area immediately to the west of Sample Location 11, between the former discharge area and the roadway (See Figure 1). A sample of this material was found to contain 1,100 mg/kg of PGDN. Such organic materials would be expected to absorb and retain PGDN effectively.

Sediment samples were collected on 15 August 1986, from the inverts of all accessible manholes in the storm sewer system downstream from the catch basin where the runoff stream enters. Manhole #3, some 300 ft westward from the catch basin which receives the runoff stream, was the only one of the sampling locations which had a sump bottom. Its sample contained 760 ug/L of PGDN, which is interpreted as the net result of 300 mg/L of soil particles containing 2,500 mg/kg PGDN. None of the other storm sewer sediment samples contained PGDN.

Additional sediment samples (T-1 and T-2) were collected on 16 October 1986 from the upstream and downstream ends of the first culvert for the runoff stream, just to the west of the point where the stream emerges from the wooded area. The culvert is about half filled with sediment. Neither of these sediment samples had a detectable concentration of PGDN.

PGDN had been detected in only two of the samples of sediments and organic debris from the runoff stream (See Section 3). It is believed that erosion gradually displaces particles containing PGDN further and further from the former discharge area. Cyanides would be present in the erosion-displaced particles, but at very low concentrations. Accordingly, the samples of sediments and organic debris from the culvert and the storm sewers were not tested for cyanides.

Table 2

## Summary of Surface Water and Sediment Monitoring Data

Location	Date	Concentrations		Flow
		PGDN	Total CN	
-----				
Surface Water Runoff Stream				
-----				
at Culvert	16 Sept	--	1.2 mg/L	3 gal/day
	24 Sept	--	0.3 mg/L	1760 gal/day
Air Cond	16 Sept	--	BDT	12 gal/min
Effluent	24 Sept	--	BDT	15 gal/min
-----				
Runoff Stream Debris		1100 mg/kg	--	
-----				
-----				
Runoff Stream Sediments (inside culvert)				
-----				
T-1 (upstream)	16 Oct	BDT	--	
T-2 (dnstream)	16 Oct	BDT	--	
-----				
Storm Sewers				
-----				
Catch Basin	15 Aug	BDT	--	
Manhole #1	15 Aug	BDT	--	
Manhole #2	15 Aug	BDT	--	
Manhole #3	15 Aug	760 ug/L	--	
Manhole #4	15 Aug	BDT	--	
Manhole #5	15 Aug	BDT	--	
Manhole #6	15 Aug	BDT	--	
Manhole #7	15 Aug	BDT	--	

Note: -- = not analyzed

BDT = below detection limits:

Total CN 0.005 mg/L in surface water stream

PGDN 25 mg/kg in runoff stream debris and sediments

PGDN 60-80 ug/L in storm sewer sediments



## 5. GROUND WATER STUDY

In August 1986, TRW authorized a study to assess potential migration of PGDN and Cyanide from the original affected area near Building 49 through surface water and ground water. This section deals with the assessment for ground water water.

The principal findings of the ground water study are as follows:

- o The lateral ground water flow below and adjacent to the former discharge area is generally from north to south.
- o Cyanide was not observed in any wells at detectable concentrations. Therefore, migration away from the Building 49 area via shallow ground water movement is not occurring.

Details follow on the methods for the ground water study and what led to these findings.

### 5.1 INSTALLATION OF GROUND WATER MONITORING WELLS

Five (5) shallow ground water monitoring wells were installed along the boundaries of the formerly swampy area south of Building 49. The wells were located 25 to 75 feet beyond the area of soil sampling of the former discharge area (see appended Drawing 6), with the major objective to determine whether cyanides are migrating out of this area via the ground water. (Otto Fuel residue was not of concern for ground water, owing to its immiscibility with water.) The monitoring wells were required to sample the shallow ground water for cyanides and to identify the approximate directions of lateral flow.

The wells were installed on 5 and 8 September 1986 by Lake Drilling Co., under the direction of Engineering-Science (ES). During the well installation, the drilling augers were cleaned between holes to eliminate cross-contamination, and undisturbed 24-inch length Shelby-tube samples of the unconsolidated sediments were obtained almost continuously down to the bedrock surface (The Shelby-tube samples were discussed in Section 3.4). The wells were completed to a depth 14 ft below the surface, and screens were installed in the bottom 10 ft. Stainless steel well casing and screen were used to ensure representative ground water samples and to ensure well

intergrity over extended time. After completion, the wells were developed by bailing and surging to remove fine-grained sediments. The well logs are included as Appendix B.

## 5.2 SAMPLING GROUND WATER

The ground water monitoring wells were sampled twice, first on 17 September and again on 9 October 1986. Each time, the wells were bailed of three to five volumes of water with a clean Teflon® bailer. In all cases, the wells recovered to static levels within a few hours. The samples were placed on ice immediately and delivered to the laboratory.

Cyanide was not detected in any of the five well samples on either sampling date. The detection limit was 0.005 mg/L, about one percent of the concentrations observed in the runoff stream.

## 5.3 GROUND WATER FLOW DIRECTION

The geology at the TAPCO complex in Euclid is typical of areas on the south shore of Lake Erie. Lacustrine silts and clays overlie weathered and fractured gray and brownish shales of Devonian age. At this location, the depth to bedrock varies from 3 to 5 ft.

Table 3 summarizes the observed water levels at the five ground water monitoring wells on two separate occasions during late September and early October 1986. On both of these observations, the water level was between 2.7 and 4.0 feet below grade, above the weathered bedrock interface. This thin weathered zone is the first saturated zone below the site.

Each time, the ground water flow was observed to be from North to South, the same direction as the surface runoff stream for the former discharge area (See appended Drawing 6). Shallow ground water flow would ordinarily be expected to follow a south-to-north gradient toward Lake Erie, following the regional surface topography. Where a surface runoff channel has cut into the topography, the ground water flow pattern may be slightly altered. In this area, the very shallow ground water may be induced to flow into this channel, thereby interrupting the overall south to north flow. Because shallow ground water is so close to the surface, it is likely that surface water and ground water are hydraulically connected.

Table 3

## Monitoring Well Data

Well Number	W-1	W-2	W-3	W-4	W-5
date installed	05-Sep	05-Sep	08-Sep	08-Sep	08-Sep
Coordinates (ft)					
North	198	25	-63	212	63
East	123	106	-5	19	-5
Elevations (ft)					
Cover	99.3	100.5	100.4	99.7	99.9
Surface	97.7	99.1	98.9	98.3	98.5
Top of Clay	96.7	96.6-98.1	96.9	92.8-98.3	96.5-97.5
Top of Screen	93.7	95.1	94.9	94.3	94.5
Shale Interface	93.2	93.6	92.9	92.8	91.9

## 24-Sep-86 Well Level Monitoring (ft)

	*				
Depth to Water	5.1	5.2	4.1	5.6	5.5
Ground Water Level	94.2	95.3	96.3	94.1	94.4

## 09-Oct-86 Well Level Monitoring (ft)

	*				
Depth to Water	4.8	4.7	4.2	5.3	5.2
Ground Water Level	94.5	95.8	96.2	94.4	94.7

## Cyanide Concentrations in Monitoring Samples (mg/L)

17-Sep-86	BDT	BDT	BDT	BDT	BDT
09-Oct-86	BDT	BDT	BDT	BDT	BDT

Note: BDT = below detection limit (0.005 mg/L Total Cyanide)

Datum for elevations 100.0 ft = floor level in Building 49

\*

Depth indicated is in feet below the top of the cover

## 6. RECOMMENDATIONS FOR CLOSURE PLAN

An assessment of risks to human health was carried out for the residues of the chemical discharges from Building 49, using very conservative established procedures to identify any potential risk to public health. [3] The Risk Assessment is included in this report as Appendix C. The methodology provides a basis for ranking of the alternatives for remedial action for the former discharges of Otto Fuel residue and cyanides near Building 49, by systematic evaluation of the possible threats to public health. This involves an understanding of the nature of the chemicals, the potential pathways for exposure of human populations in the event of any future release from the site, the degrees to which such releases (if any) could violate applicable standards and criteria, and a measure of the potential threats to public health that might result from such releases.

The principal findings in this Risk Assessment are as follows:

- o The no-action alternative is not recommended. Soil containing Otto Fuel residue and cyanides is a hazard to public health, posing an ongoing ingestion, inhalation and dermal contact danger. It would continue to be subject to mobilization by particle erosion, eventually discharging through the storm sewer system (into Lake Erie). Cyanides would continue to leach into the runoff stream in detectable, but low concentrations, posing a threat until chemical degradation, volatilization, bacterial action and/or plant uptake eventually mitigate the hazards due to cyanides.
- o The minimum action required would be to remove soils containing detectable Otto Fuel residue and cyanide concentrations exceeding 10 mg/kg, at the former discharge pipe and in the runoff stream, with due precautions to avoid mobilization during removal.
- o Ultimate disposal of the soil removed from the areas of highest concentrations should be by incineration.

- o No further removal of soil from the area would be required. Although cyanides would be present, at concentrations less than 10 mg/kg, there would be no remaining significant threats to public health. The alternative of additional soil removal and disposal at an industrial landfill (not certified for hazardous materials containing cyanides) would not achieve significantly improved reduction of hazards.

Details of the Risk Assessment are found in Appendix C. These issues, and the implications for Closure of the Building 49 area, are addressed in the sections that follow:

#### 6.1 CLOSURE OF THE SPILL AREA

Surface soil in the approximately 625 sq.ft polygon area noted on Figure 5 and the runoff stream channel will have to be excavated for off-site disposal. This will remove all areas with detectable PGDN concentrations and/or Total Cyanide exceeding 10 mg/kg. It is recommended that the removal should include the organic surface soils and the upper 1 ft. of clay. Assuming a total depth of 4 ft. removed from area near the former discharge pipe and 2 ft. x 2 ft. dredging of the 120 ft. long runoff stream, the soil removal would amount to about 100 cubic yards. The sediments in the first culvert and the sediments from all manholes in the storm sewer system will also have to be removed. The contaminated leaves and organic debris, previously removed from the runoff steam channel and dumped in the wooded area, should be collected and added to the soil and sediments.

A Gradall or a hydraulic clamshell would be required for the soil removal and stream dredging. Personnel protection would be necessary at Level B (disposable outer garments and respiration equipment). However, mechanical methods, i.e., working upwind or use of fans would minimize the need for supplied air (See Appendix C).

Site work will be required, to provide access to the removal area for earthmoving equipment. A 12 ft. wide temporary roadway using 9" to 12" coarse stone and construction filter fabric is recommended. This should follow a southward alignment on the east side of Building 49, through the existing fence, and westward to the removal area (See appended Drawing 7).

Additional site work should also be considered, to change the drainage to the runoff stream. A new drainage channel is proposed, which would follow a semi-circular arc from the low point in the ponding area, south-westward to join the existing runoff stream near the culvert (See appended Drawing 7). This would decrease leaching of cyanides into the runoff by preventing the ponding that now provides extended contact time. It will also reduce flow through the runoff stream, thereby reducing further migration by erosion of any contaminated sediment particles in the stream channel.

## 6.2 CONCENTRATION LIMITS FOR RESIDUES IN THE SOIL

The recommended action, to excavate soil near the former discharge pipe and to dredge the bed of the runoff stream, will remove all Otto Fuel residues detected in the soil sampling (See Figures 5 and 6). This conforms to the recommendation for off-site disposal of soil containing Otto Fuel from spills, in the U.S. Navy manual for Otto Fuel [1]. The Risk Assessment (Appendix C) identified toxic hazards to public health associated with the Otto Fuel Residues.

This action would also remove the soil with the highest cyanide concentrations, which occurred in essentially the same areas. After the removal, Cyanides will be present at concentrations not exceeding 10 mg/kg anywhere in the area. This is more stringent than the 20 mg/kg recommended preliminary cleanup target concentration for cyanides in soil [4]. The Risk Assessment indicates that the remaining soil, being free of PGDN and containing low concentrations of cyanides, should not be considered harmful. Natural soils under aerobic conditions are known to be tolerant of (and capable of assimilating) cyanides at concentrations exceeding 2 mg/kg [5].

Recent actions by State agencies with respect to cyanides in mineral processing residues have required removal to levels up to 10 mg/kg, based on rationale for the cyanide concentrations that would leach into surface water [6]. For example, the California Regional Water Quality Control Board, Colorado River Basin, Region 7 increased the limit on total cyanide found in abandoned leach piles from 1.0 mg/kg to 10 mg/kg, after a review of fish toxicity studies and the environmental chemistry of cyanides. Their rationale was that only the cyanide ion content has to be considered.

A cyanide level of 0.02 mg/L was acceptable in the receiving stream, and after multiplying by their customary factor of 100 to account for dilution, a level of 2.0 mg/L was obtained for the leachate. Then, the acceptable limit for a solid residue is 10 mg/kg based on leaching 1 part solid: 5 parts liquid [5].

The runoff stream from the former discharge area south of Building 49 was observed to contain from 0.24 to 1.2 mg/L of Total Cyanide. Leaching of cyanides into this stream is predicted to decrease by about 70 percent after the recommended removal of all soil and sediments containing detectable PGDN and Total Cyanides exceeding 10 mg/kg. Even discounting any further dilution, the predicted 0.07 to 0.36 mg/L (70 to 360 ug/L) concentrations in the runoff stream would be within the 700 ug/L preliminary cleanup target concentration for cyanides in water [4].

### 6.3 ULTIMATE DISPOSAL OF SOIL

The U.S. Navy manual for Otto Fuel [1] recommends off-site disposal for soil containing Otto Fuel from spills. Concentrated liquid residues of Otto Fuel are presently disposed of by incineration. (As supplied, Otto Fuel is considered by the Navy and by Navy contractors as subject to RCRA regulations as a reactive hazardous material.) Rotary-kiln incinerators would have to be used, since liquid hazardous waste incinerator installations generally can only handle limited quantities of drummed soil. The costs for disposal by incineration will be high, since there may be problems with ash disposal and/or material handling (size reduction, moisture content, etc.) depending on site-specific requirements of the installation to be used.

The manual does describe a method for chemical reduction of liquid Otto Fuel residues, using acetone solvent and sodium sulfide. [1] This does not appear to be feasible for on-site application, since it would require rigorous working area isolation facilities to ensure personnel safety and to prevent emission of toxic hydrogen sulfide fumes.

Depending on the quantity of soil involved, on-site chemical destruction of cyanide may be economically feasible in comparison to landfill disposal. The technology for alkaline hypochlorination of excavated soil using earth moving equipment was estimated by its developers (Haztech) to cost in the range of \$50 to \$150/cu.yd., for soil quantities of 250 to 500

cu.yd. This method has been used at two sites which had experienced spillage of concentrated cyanides, to treat soils containing 100 mg/kg or more of cyanides. It is claimed to be capable of reducing cyanides to concentrations below present detection limits, at somewhat higher costs. Preventing emission of toxic chlorine fumes during the soil treatment is a major drawback for this technology.

An optional alternative for site work could also be considered, to inter the remaining cyanides insitu, by regrading to provide an impermeable cap over the areas containing detectable cyanides and diverting all surface runoff and ground water that would otherwise contact the buried soil. However, this would involve a commitment to long-term monitoring of ground water quality.

#### 6.4 CLOSURE OF BUILDING 49 AND THE ADJOINING AREA

The entire Torpedo Test area should undergo closure at the same time as the spill area. Additional activities that should be included in the Closure are discussed in the paragraphs that follow:

Leakage of torpedo test wastewater may have occurred from the underground tanks and piping. In order to locate such leakage sites, if any, the 1,000 gallon underground separator tank for wastewater discharges from Building 49 must be removed, and the former discharge piping should be unearthed along its entire length (estimated to be about 60 ft). Similarly, the new underground holding tanks for torpedo test wastewater, which were installed on the west side of Building 49, and the piping from the separator tank to the new holding tanks must also be removed.

Soil sampling and analysis for PGDN should be carried out at the tank sites and along the piping, at the pipe joints and any other suspect locations. In addition, the soil at two areas of possible spillage of Otto Fuel or torpedo testing wastewater should also be sampled and analyzed for PGDN. Spills may have occurred at the Otto Fuel Storage area on the east side of Building 49 and/or on the concrete pad on the south side of the building.

The tanks and pipe should be cleaned on site by rinsing with detergent solution (Wisk), and the spent rinses should be collected for disposal by incineration. Samples of the last spent rinses should be analyzed for PGDN to verify that no Otto Fuel residues remain. The tanks may then be



salvaged for reuse, if possible, or disposed of as non-hazardous solid waste.

In the event that Building 49 or any of the auxiliary buildings are to be demolished in the foreseeable future, it would be prudent to test at this time for asbestos insulation. Similarly, transformers in the torpedo testing compound should be checked for PCBs.

The soil mound between Building 49 and the former discharge area has been sampled and analyzed for cyanides. It was found to be free of cyanides, hence this soil can be used for backfilling after removal of soil containing residues of PGDN and cyanides.

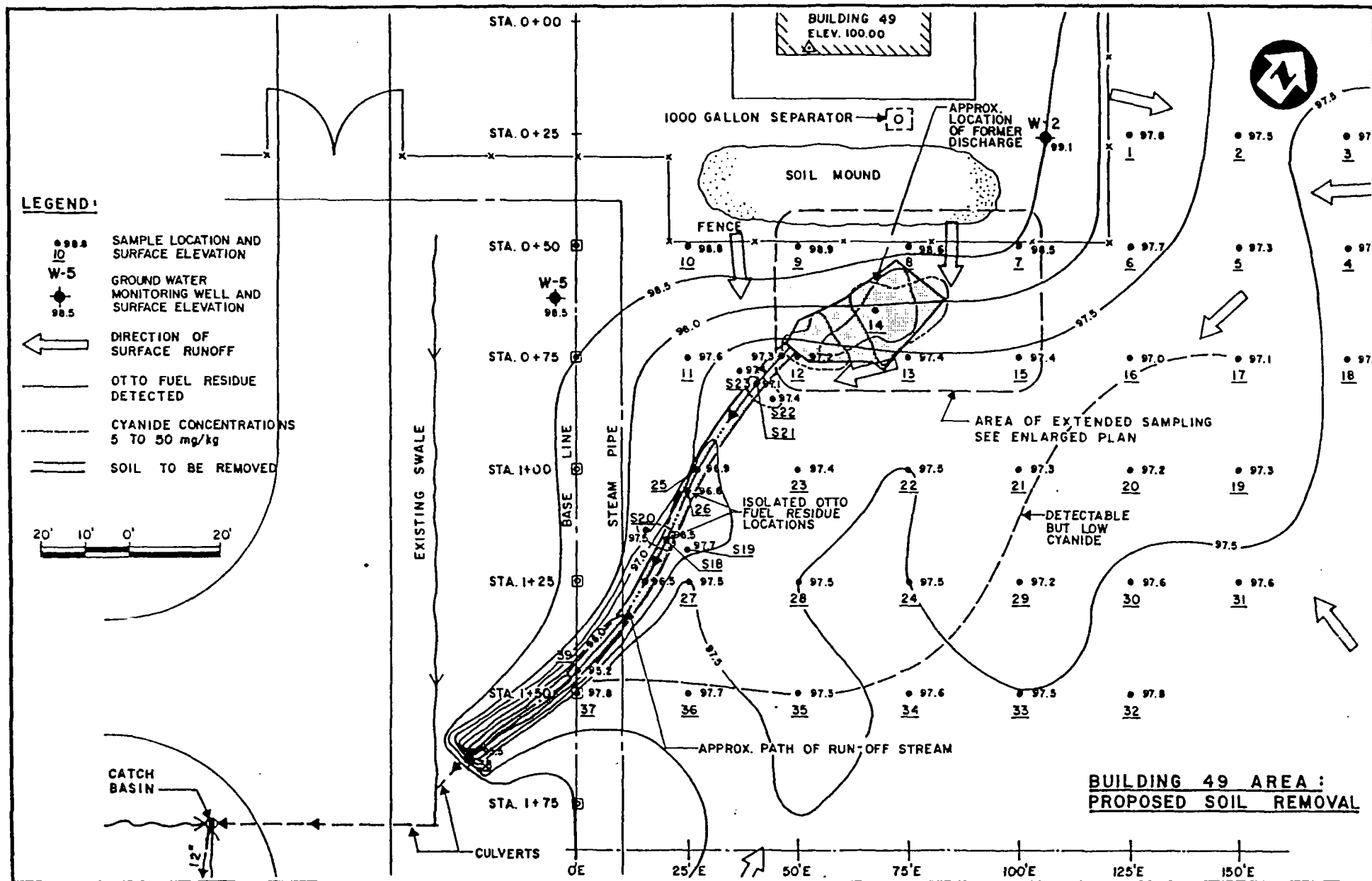
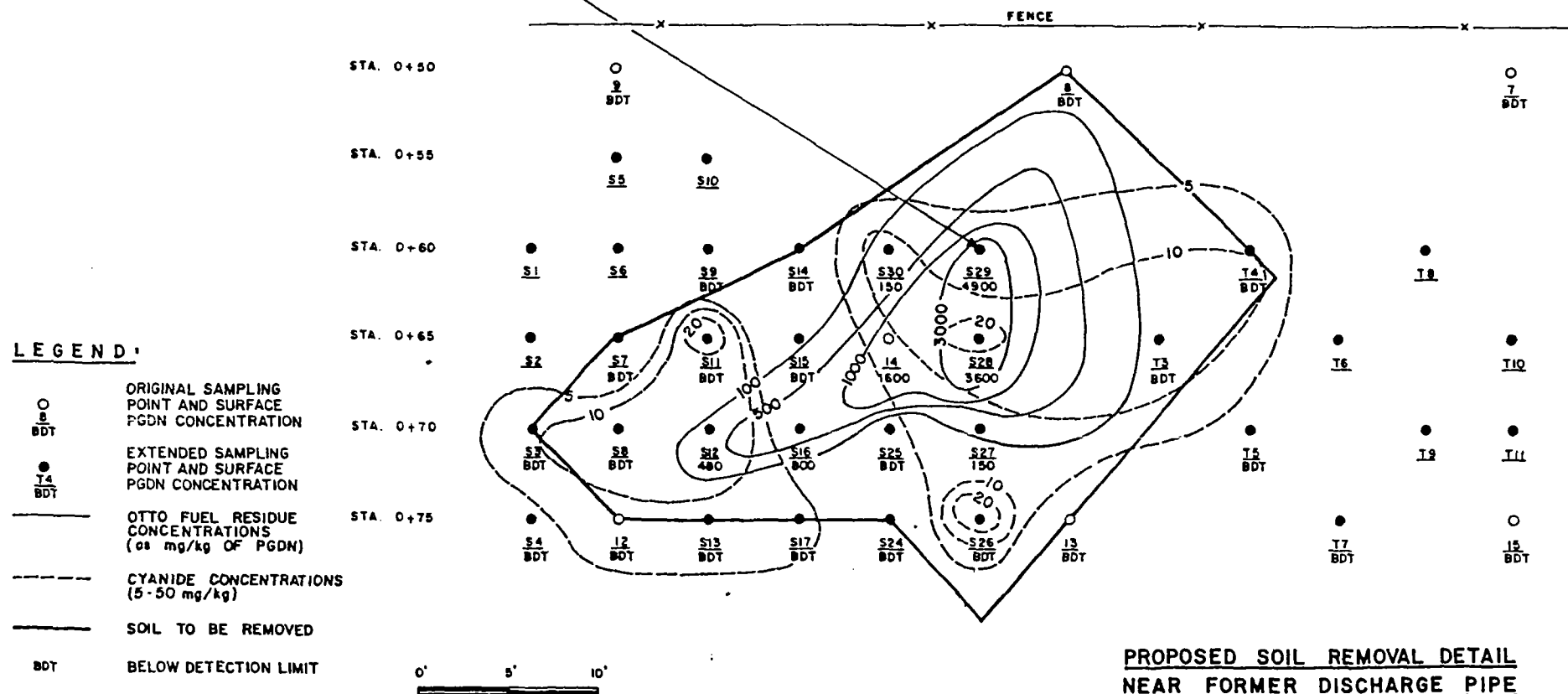


FIGURE 5

NOTE: PGDN 80mg/kg 2' DEPTH  
TO BOTTOM OF CORE  
AT S29 PGDN BDT BELOW  
1FT. AT ALL OTHER  
LOCATIONS TESTED



## REFERENCES

1. Technical Manual: OTTO Fuel II Safety, Storage and Handling, 6th Revision, NAVSEA OP 3368 (U.S. Navy Sea Systems Command, 1 October, 1976).
2. Test Methods for Evaluating Solid Wastes: Physical and Chemical Methods, SW-846, Second Edition (Revised), U.S. Environmental Protection Agency, Office of Solid Wastes, 1984.
3. Superfund Public Health Evaluation Manual, OSWER Directive 9285.4-1, Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C., October 1986.
4. Surface Impoundment Clean Closure Guidance Manual, OSWER Directive 9476.00-8.C., Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C., October 1987.
5. Fuller, W.H., "Cyanides in the Environment, with Particular Attention to the Soil", keynote review paper presented at Conference on Cyanide and the Environment, Tucson, AZ., Dec. 1984, pp.19-45.
6. Engineering-Science, Inc. (ES), "Cyanide Chemistry" excerpt from report to U.S. Environmental Protection Agency, Water Management Division, State Programs Branch, Denver, CO., 1986. "Heap Leach Technology and Potential Effects in the Black Hills", pp. 283-340, (See Table B-11, "Western State Regulations or Guidelines for Neutralization of Spent Heap Leach Piles", pp. 326-327.)

NOTE: Reprints are provided of References [5] and [6], in Appendices D and E, respectively.

APPENDIX A

HEALTH AND SAFETY PLAN FOR BUILDING 49 STUDY

# **ES** ENGINEERING-SCIENCE

57 EXECUTIVE PARK SOUTH, N.E., SUITE 590 • ATLANTA, GEORGIA 30329 • 404/325-0770

66207/864J50

April 7, 1986

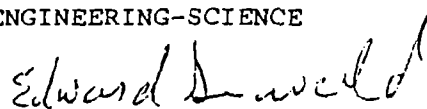
Chris Raddel  
Engineering-Science, Inc.  
19101 Villaview Road  
Suite 301  
Cleveland, Ohio 44119

Dear Chris:

Please find enclosed the Safety Guidelines for the TRW site investigation. If you have any comments concerning any of the protocols feel free to contact me.

Sincerely,

ENGINEERING-SCIENCE



Edward Grunwald  
Corporate Health and Safety  
Manager

EG/bb

Enclosure

### Respiratory Protection

The personal levels of respiratory protection prescribed for the field work to be performed at TRW building 49 is level D with a contingency to use level C. This level is based upon the potential exposure to OTTO. OTTO is a monopropellant made up of 1,2-propylene glycol Dinitrate, Di-N-butyl Sebacate, and 2-Nitrodiphenylamine. OTTO has a very low vapor pressure, therefore, the inhalation of toxic gases, fumes, or vapors is unlikely to be encountered. The inhalation of toxic particulates (dusts, soils, etc.) can be a problem when soil conditions are dry. If the inhalation of airborne particulates is a problem, (as may be the case during drilling activities) field personnel should "water down" the area of concern. OTTO does not have an established Threshold Limit Value (TLV) or Permissible Exposure Limit (PEL). The major component of OTTO, 1,2-Propylene Glycol Dinitrate, has a TLV of 0.02 ppm. Because of the low TLV of 1,2-Propylene Glycol Dinitrate ambient air monitoring of organic vapors will be required at each sampling point and drilling location. This information will be used to aid the site manager in determining the level of protection for the various activities.

The following criteria should be used to select the appropriate respiratory protection:

<u>Organic Vapor Concentration</u> <u>(in Breathing Zone)</u>	<u>Protection Level</u>
0 PPM	Level D
0.02-5 PPM	Level C

Level C respiratory protection should not be used for protection with poor warning properties or in an atmosphere containing less than 19.5 percent oxygen (ANSI Z88.2-1980). Information is not available to determine if OTTO had good warning properties (i.e., low odor threshold

when compared to its TLV). For this reason the upper limit for level C respirator protection is set at 5 ppm, at this concentration cartridge breakthrough is unlikely to occur. Level C respiratory protection will consist of a full face air mask with organic vapor cartridges. Individuals who use air purifying respirators must wear a respirator which has successfully been fitted to their faces. An improperly fitted respirator delivers little respiratory protection. Additionally, a five minute escape air pack must be available when Level C operations commence.

Level B respiratory protection Self-Contained Breathing Apparatus (SCBA) will be worn when the following conditions occur:

- o When organic vapor concentration (in the breathing zone) exceeds 5 PPM
- o When evidence exists of immediate (less than five minutes) breakthrough time for the cartridge air-purifying respirator.
- o Where there is reason to suspect that the cartridge sorbent has a high heat of reaction (hot to the touch) with one of the substances at the site.
- o Where there is reason to suspect that a substance sorbed onto the surface of a cartridge is shock sensitive.

#### Dermal Protection

OTTO can be absorbed through the skin; OTTO is also an eye irritant. Personnel can avoid skin and eye contact by wearing the protective clothing specified below.

For level D Operations:

- o Tyvek or Saranex suits (over coveralls)
- o Neoprene boots
- o Polyethylene gloves
- o Goggles

For Level C Operations



- o Full-face air purifying respirator equipped with organic vapor cartridges
- o Neoprene outer gloves
- o Polyethylene inner gloves
- o Tyvek or Saranex suits (over coveralls)
- o Steel-toed Neoprene boots

#### Health and Safety Training

Every potential respirator wearer shall receive fitting instructions including demonstrations and practice in how the respirator should be worn, how to adjust it, and how to determine if it fits properly.

#### Air Monitoring

Monitoring for organic vapors will be conducted using an HNu with an 11.7 ev lamp. Reading of organic vapor concentration above background will initiate Level C respiratory protection.

#### Health and Safety Equipment

Each field team shall have the following items readily available:

- o Copy of site Health and Safety Plan including a list of emergency contacts
- o First aid kit
- o Eye wash bottle
- o Duct tape
- o Paper towels
- o Plastic garbage bags
- o HNu with 11.7 ev lamp
- o Long-handle brushes
- o Tyvek
- o Gloves
- o Full-face air purifying respirator
- o Safety boots
- o Decon solution
- o Organic vapor cartridges

## SITE SPECIFIC DECONTAMINATION PROCEDURES

Work at the TRW site will be of moderate duration and exposure to hazardous materials should be minimal if proper precautions are followed. Simple and expedient decontamination procedures, appropriate to the site and work conditions, will be followed.

Based upon the site information, it may be necessary to establish one or more zones of exclusion. Should this occur, a decontamination pad will be established at the entrance/exit point to each exclusion zone. Workers entering this area must be equipped in the level of protection previously established. The decontamination procedures must be followed by all personnel as they leave the zone of exclusion.

Level C decontamination at the TRW site will consist of the following:

### Station 1: Segregated Equipment Drop

Deposit equipment used on the site (tools, sampling devices and containers, monitoring instruments, clipboards, etc.) on plastic drop cloths or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross-contamination.

Equipment necessary is:

1. Containers of various sizes
2. Plastic liners
3. Plastic drop cloths

### Station 2: Suit/Safety Boot and Outer-Glove Wash

Thoroughly wash tyvex or saranex suit, safety boots and outer-gloves. Scrub with long-handle, soft-bristle scrub brush and copious amount of decon solution (Wisk®/water solution). Repeat as many times as necessary (determined by visual inspection).

Equipment necessary is:

1. Container (30 gal)
2. Decon solution: Wisk®/water solution
3. Long-handle, soft-bristle scrub brushes

Station 3: Suit/Safety Boot and Outer-Glove Rinse

Rinse off decon solution (Wisk®/water solution) using copious amount of water. Repeat as many times as necessary.

Equipment necessary is:

1. Container (30 gal)
2. Spray unit
3. Water
4. Long-handle, soft-bristle scrub brushes

Station 4: Canister or Mask Change

If worker leaves Exclusion Zone to change canister (or mask), this is the last step in the decontamination procedures. Worker's canister is exchanged, new outer gloves and tyvec donned, and joints taped. Worker returns to duty.

Equipment necessary is:

1. Canister (or mask)
2. Tape
3. Boot covers
4. Gloves

Station 5: Outer Glove Removal

Remove outer gloves and deposit in individually marked plastic bags.

Equipment necessary is:

1. Container (30 gal)
2. Plastic liners
3. Bench or stool

Station 6: Tyvex or Saranex Suit Removal

With assistance of helper, remove tyvex or saranex suit. Deposit in container with plastic liner.

Equipment necessary is:

1. Container (30 gal)
2. Stool
3. Plastic liner

Station 7: Inner-Glove Wash

Wash inner-gloves with Wisk®/water solution that will not harm skin. Repeat as many times as necessary.

Equipment necessary is:

1. container
2. water
3. wash basin
4. brushes

Station 8: Inner-Glove Rinse

Rinse inner-gloves with water. Repeat as many times as necessary.

Equipment necessary is:

1. Water
2. Basin
3. Small table

Station 9: Safety Boot Removal

Remove safety boots and deposit in individually marked plastic bags.

Equipment necessary is:

1. Container
2. Plastic liners
3. Bench or stool

Station 10: Respirator Removal

Remove facepiece. Avoid touching face with gloves. Wash respirator in clean, sanitized solution (e.g., antiseptic mouthwash) and deposit facepiece in plastic bag. Store in clean area.

Equipment necessary is:

1. Plastic bags

Station 11: Inner-Glove Removal

Remove inner-gloves and deposit in container with plastic liner.

Equipment necessary is:

1. Container
2. Plastic liners

Station 12: Field Wash

Wash hands and face.

Equipment necessary is:

1. Water
2. Soap
3. Tables
4. Wash basins or buckets

#### Equipment Decontamination

The drill rigs and downhole equipment will be steam cleaned prior to drilling the first boring. Downhole equipment will be decontaminated after the completion of each boring in the following manner:

- o Downhole equipment (auger bits, drill rods, etc.) will be steam cleaned to remove gross contamination;
- o The equipment will then be washed in a detergent (Wisk®) solution and brushed.
- o The equipment will then be rinsed with tap water, followed by acetone and distilled water.
- o The downhole equipment will then be air dried in a clean section of the decontamination area.

Drill rigs will be steam cleaned upon the completion of the final boring. A drilling sequence hierarchy (from less likely to more likely contaminated boring locations) will be imposed to reduce the potential of cross contamination.

#### Hazard Evaluation

The compound of concern at the TRW site is OTTO. Although this chemical has a low vapor pressure air monitoring for organics should be conducted (particularly during drilling activities) to determine the need to upgrade the level of respiratory protection. Since OTTO is a propellant care should be taken to use non-sparking tools whenever possible. Smoking will be prohibited at the site. An explosimeter may

be a useful tool for monitoring combustible atmospheres when the chemical of concern is volatile but in the case of OTTO which is a non volatile, viscous substance the benefit gained by using an explosimeter is questionable.

The toxic effects from the inhalation of OTTO include: headaches, nasal congestion, and a drop in blood pressure. OTTO is also an eye irritant. The proper selection of protective clothing is important. Polyethylene and Neoprene clothing (gloves and boots) provide the greatest degree of protection. Butyl rubber and natural rubber tends to degrade quicker when exposed to the components of OTTO. Neoprene gloves and boots are recommended as a substitute for natural rubber garments.

APPENDIX B

WELL LOGS

GROUND WATER OBSERVATIONS		Weather	Surface Elev.
AT	AFTER	Remarks	Date Start
FT.	HOURS		
AT	AFTER		Date Finish
FT.	HOURS		

D = DRY            W = WASHED            C = CORED            P = PIT            A = AUGER CUTTINGS U = UNDISTURBED            SS = SPLIT SPOON					PAY QUANTITIES	
					FOOTAGE IN EARTH	5
					FOOTAGE IN ROCK	10
					NO. OF SAMPLES	2
					CORE BARREL	0



DRILLING CONTRACTOR:  
 Driller: LAKE DRILLING  
 Inspector: K.M. Palumbo

ENGINEERING-SCIENCE  
 DRILLING RECORD

BORING NO. W-2  
 Sheet 1 of 1  
 Location \_\_\_\_\_

PROJECT NAME TRW Building 49 Study  
 PROJECT NO. CL021

GROUND WATER OBSERVATIONS

AT \_\_\_\_\_ FT. AFTER \_\_\_\_\_ HOURS

AT \_\_\_\_\_ FT. AFTER \_\_\_\_\_ HOURS

Weather Sunny 70's  
 Remarks Screen Size .010  
STAINLESS STEEL

Surface Elev. \_\_\_\_\_  
 Date Start 9-5-86  
 Date Finish 9-5-86

DEPTH BELOW SURFACE	SAMPLE DEPTHS	TYPE OF SAMPLE	STANDARD PENETRATION TEST			STRATA CHANGE	REMARKS  FIELD IDENTIFICATION OF MATERIAL (Incl. Color, Loss of Wash Water, Seams in Rock, etc.)	WELL CONSTRUCTION DETAILS
			0-6	6-12	12-18			
							Brown Sandy Topsoil	<div style="text-align: center;">Ground Surf.</div> <div style="text-align: center;">Protective cover</div>
						1		
							Light Brown Silty Clay	
						2.5		
							Dark gray to Black clay (Appears Stained)	
						3.5		
							Brown weathered clay with shale fragments	
						5.5		
							Weathered, fractured Gray shale.	
						11		
							Harder gray shale.	<div style="text-align: center;">COARSE SA</div> <div style="text-align: center;">X X</div> <div style="text-align: center;">X X</div>

D = DRY      W = WASHED      C = CORED      P = PIT      A = AUGER CUTTINGS

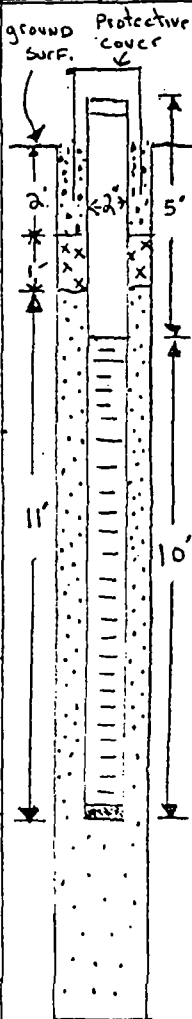
U = UNDISTURBED      SS = SPLIT SPOON

PAY QUANTITIES

FOOTAGE IN EARTH	5.5
FOOTAGE IN ROCK	11.5
NO. OF SAMPLES	2
CORE BARREL	0

DRILLING CONTRACTOR: Filler: <u>LAKE DRILLING</u> Director: <u>K.M. Palumbo</u>	<b>ENGINEERING-SCIENCE DRILLING RECORD</b>	BORING NO. <u>W-3</u> Sheet <u>1</u> of <u>1</u> Location _____ _____ _____
PROJECT NAME <u>TRW Building 49</u> PROJECT NO. <u>CLO21</u>		

<b>GROUND WATER OBSERVATIONS</b>  AT _____ FT. AFTER _____ HOURS  AT _____ FT. AFTER _____ HOURS	Weather <u>PTLY Cloudy - Cool 60's</u> Remarks <u>Screen Size .010</u> <u>STAINLESS STEEL</u>	Surface Elev. _____ Date Start <u>9-8-86</u> Date Finish <u>9-8-86</u>
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DEPTH BELOW SURFACE	SAMPLE DEPTHS	TYPE OF SAMPLE	STANDARD PENETRATION TEST			STRATA CHANGE	REMARKS  FIELD IDENTIFICATION OF MATERIAL (Incl. Color, Loss of Wash Water, Seams in Rock, etc.)	WELL CONSTRUCTION DETAILS
			0-6	6-12	12-18			
							Top soil - Light Brown Silt w/minor Fine Sand	
						1	GRAVEL, OLD ASPHALT, WOOD (Fill)	
						2	DARK GRAY clay. (appears stained, hydrocarbon odor)	
3.0-5.0	u					3.5	MEDIUM BROWN Silty Clay	
						6.0	Brown weathered Shale	
						6.5	Gray, weathered, (broken) Shale	
						16	Gray Shale, harder, less weathered	
						18		
							<div><div><div></div><div></div><div></div></div>COARSE SAND</div> <div><div><div></div><div></div><div></div></div>BENTONITE</div> <div><div><div></div><div></div><div></div></div>CEMENT</div>	

D = DRY    W = WASHED    C = CORED    P = PIT    A = AUGER CUTTINGS U = UNDISTURBED    SS = SPLIT SPOON	<b>PAY QUANTITIES</b>
	FOOTAGE IN EARTH <u>6.0</u> FOOTAGE IN ROCK <u>17.0</u> NO. OF SAMPLES <u>2</u> CORE BARREL <u>1</u>

GROUND WATER OBSERVATIONS		Weather _____ Remarks _____	Surface Elev. _____ Date Start _____ Date Finish _____
AT ____ FT.	AFTER ____ HOURS	<u>Ptly Cloudy, cool 60's</u>	<u>9-8-86</u>
		<u>Screen Size .010</u>	<u>9-8-86</u>
		<u>STAINLESS STEEL</u>	
AT ____ FT.	AFTER ____ HOURS		

D = DRY      W = WASHED      C = CORED      P = PIT      A = AUGER CUTTINGS U = UNDISTURBED      SS = SPLIT SPOON					PAY QUANTITIES	
					FOOTAGE IN EARTH	5.5
					FOOTAGE IN ROCK	11.5
					NO. OF SAMPLES	2

Concentrations (detectable only in the top 1 ft of sample cores) -  
approximately 300 ft<sup>2</sup> area near the former discharge pipe site:

average of all detectable concentrations = 1900 mg/kg  
maximum concentration observed = 4900 mg/kg

in the runoff stream sediments:

average of the two isolated samples with  
detectable concentrations = 160 mg/kg  
maximum concentration observed = 240 mg/kg

Cyanides, which are present as a result of incomplete combustion of Otto Fuel in torpedo testing, are characterized as follows:

Mobility - Cyanides, being generally soluble in water, are capable of leaching either into surface runoff or into ground water flow. Cyanide concentrations of 0.24 to 1.2 mg/L were observed in the actual runoff stream flow.

Toxicity - Cyanides are notorious for toxicity to humans and animals, due to interference with oxygen metabolism.

Persistence - Cyanides do degrade in the environment. Under acidic conditions, cyanides are converted to the volatile hydrocyanic acid (HCN) and released to the atmosphere. Other mechanisms of cyanide degradation, including ultraviolet light, bacterial action, and direct uptake by plants are known to occur [4].

Concentrations in the top 1 ft of sample cores) - (note that detectable, but generally much smaller concentrations are present further below the soil surface)

approximately 1,000 ft<sup>2</sup> area near the former discharge pipe:  
average of all detectable concentrations = 10 mg/kg  
maximum concentration observed = 54 mg/kg

DRILLING CONTRACTOR: Filler: <u>LAKE DRILLING</u> Inspector: <u>K.M. Palumbo</u>	<b>ENGINEERING-SCIENCE DRILLING RECORD</b>	BORING NO. <u>W-5</u> Sheet <u>1</u> of <u>1</u> Location <u>10' W. OF OVERHEAD STEAM LINES</u>
PROJECT NAME <u>TRW BUILDING 49 STUDY</u> PROJECT NO. <u>CLOZ1</u>		

GROUND WATER OBSERVATIONS  AT <u>    </u> FT. AFTER <u>    </u> HOURS  AT <u>    </u> FT. AFTER <u>    </u> HOURS	Weather <u>PTLY CLDY 60'S</u> Remarks <u>SCREEN SIZE .010</u> <u>STAINLESS STEEL</u> <u>SCREEN AND RISER</u>	Surface Elev. <u>          </u> Date Start <u>9-8-86</u> Date Finish <u>9-8-86</u>
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DEPTH BELOW SURFACE	SAMPLE DEPTHS	TYPE OF SAMPLE	STANDARD PENETRATION TEST			STRATA CHANGE	REMARKS FIELD IDENTIFICATION OF MATERIAL (Incl. Color, Loss of Wash Water, Seams in Rock, etc.)	WELL CONSTRUCTION DETAILS
			0-6	6-12	12-18			
	1-3'	U				2	Top Soil / Brown Silty Clay	
						3	Dark gray clay - No odors	
	3.5-5	U				6	Brownish-Gray Clay MOIST AT TOP DRY AT BOTTOM	
						7	Brown firm clay to weathered shale	
						11	Gray Shale	
						12	Brownish Gray Shale (weathered, Fractured, iron stains)	
						17	Gray Shale w/ some Brown streaks	
							<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">  coarse sand         </div> <div style="text-align: center;">  BENTONITE         </div> <div style="text-align: center;">  CEMENT         </div> </div>	

D = DRY    W = WASHED    C = CORED    P = PIT    A = AUGER CUTTINGS U = UNDISTURBED    SS = SPLIT SPOON					<b>PAY QUANTITIES</b>	
					FOOTAGE IN EARTH	6
					FOOTAGE IN ROCK	11

APPENDIX C  
RISK ASSESSMENT

## APPENDIX C

### RISK ASSESSMENT

An assessment of risks to public health was carried out for the area near Building 49 affected by the discharges of Otto Fuel residue and cyanides. The assessment covered both existing conditions and alternatives for remedial action. The discussion that follows describes the Risk Assessment procedure in general terms and then applies that methodology to the case at hand.

#### 1. BASELINE RISK ASSESSMENT PROCEDURE

The methodology for assessment of risks to public health is based on very conservative established procedures to identify and evaluate the possible threats [1]. This involves an understanding of the nature of the chemicals, the potential pathways for exposure of human populations in the event of any release from the site, the degrees to which such releases could violate applicable standards and criteria, and a measure of the potential threats to public health that might result from such releases. The risk assessment consists of five steps, as follows:

STEP 1: Selection of Indicator Chemicals chooses a tractable number of chemical species from among those present, for quantitative estimates. If necessary, the indicator species should be chosen on the basis of higher mobility, greater toxicity, more persistence in the environment and/or higher concentrations. A screening procedure is available for use with complicated mixtures.

STEP 2: Estimation of Exposure Point Concentrations consists of identifying possible pathways for exposure of human populations to indicator chemical releases from the site, identifying the potential exposure points, and estimating the chemical releases and their subsequent environmental fate and transport via air, ground water, surface water and soils. Separate accountings must be made for pathways leading to oral intake, to

direct dermal intake, or to intake by ingestion, since each intake mechanism has separate toxicological data base.

The exposure pathways are reviewed to identify which of them may be "complete" pathways for exposure of human populations. An exposure pathway is comprised of a source and mechanism of chemical release; an environmental transport medium; a human exposure point and a feasible exposure route to the exposure point. If any one portion of the exposure pathway is missing, then exposure by that route is not possible.

The projected exposure levels may then be compared to Applicable or Relevant and Appropriate Requirements (ARARs), which include allowance for the intake mechanisms and the toxicological limits. If possible, determinations should be made for both acute and chronic (long-term) exposure. In the event that ARAR values are available for all indicator chemicals, it is not necessary to proceed with the remaining steps of the Risk Assessment Procedure.

STEP 3: Estimation of Chemical Intake attempts to quantify the actual human exposure, in order to assess possible adverse health effects. The exposure is expressed in terms of intake, i.e., the amount of a substance taken into the body per day, per unit body weight. Each of the media should be considered separately, due to their differing assumptions and variable data quality.

The intakes for each indicator chemical are combined separately for the oral and inhalation routes. Toxicological data generally keep these routes separate. For long-term (chronic) exposure, the oral (or the inhalation) intake rates are combined by summation. However, for the short-term (subchronic) exposure, where peak intakes are of interest, the largest individual intake for the given route would be appropriate.

STEP 4: Toxicity Assessment presents critical toxicity values for the indicator chemicals, to be used in conjunction with the results of exposure assessment for characterization of risks. The USEPA has developed a tabulation of values which describe the degree of toxicity posed by various chemicals, as follows:



acceptable intake for subchronic exposure (AIS),  
acceptable intake for chronic exposure (AIC),  
carcinogenic potency factor (carcinogens only),

The AIC and AIS values were derived from quantitative information available from animal toxicity studies and limited human epidemiological data, and stated in units of mg/kg body weight/day. The values are intended to be protective of sensitive populations. The carcinogenic potency factors have units of lifetime cancer risk per (mg/kg body weight/day).

STEP 5: Risk Characterization makes the comparison between projected intakes and reference levels for non-carcinogens. When carcinogens are present, Step 5 compares the calculated risks to target risks. This is in addition to earlier comparison of exposure point concentrations vs. applicable or relevant and appropriate requirements (ARARs) or other standards and criteria.

To assess the overall potential for non-carcinogenic effects posed by multiple chemicals, EPA developed a Hazard Index approach which assumes that multiple sub-threshold exposures may result in an adverse effect, and that the magnitude of the adverse effect will be in proportion to the summation of the ratios of the individual sub-threshold exposures (intakes) to acceptable intake levels for each chemical, i.e.,

$$\text{Subchronic Hazard Index} = (IS_1/AIS_1 + IS_2/AIS_2 + \dots)$$

$$\text{Chronic Hazard Index} = (IS_1/AIC_1 + IS_2/AIC_2 + \dots)$$

The assumption of additivity is best applied to compounds that induce the same effect by the same mechanism. Applying the Hazard Index to a mixture of compounds that are not expected to induce the same type of effects could overestimate the risk.

The Hazard Indexes are determined individually for the oral and the ingestion routes (and separately for subchronic and chronic exposures). It is not appropriate to combine the two because toxicity data are route specific.

The formal risk assessment procedure concludes with a review of site-specific factors that may increase uncertainty. Sensitive populations, such as hospitals or institutions, could require a more conservative interpretation of hazards. Exposure uncertainties and non-quantifiable exposure routes, overall data adequacy, non-indicator chemicals and chemical or biological interactions should be reviewed.

## 2. BASELINE RISK ASSESSMENT - EXISTING CONDITIONS

STEP 1: Selection of Indicator Chemicals: For the area near Building 49 affected by the discharges of torpedos testing wastewater, only two chemicals are of concern: Propylene Glycol Dinitrate (PGDN) and Cyanides.

PGDN is the principal component of Otto Fuel II, a combustible chemical in its purified form, which is stable at ambient conditions (and not flammable according to U.S. Department of Transportation criteria). It is chemically similar to Nitroglycerin and to Ethylene Dinitrate (EDN), a byproduct of Nitroglycerin manufacturing.

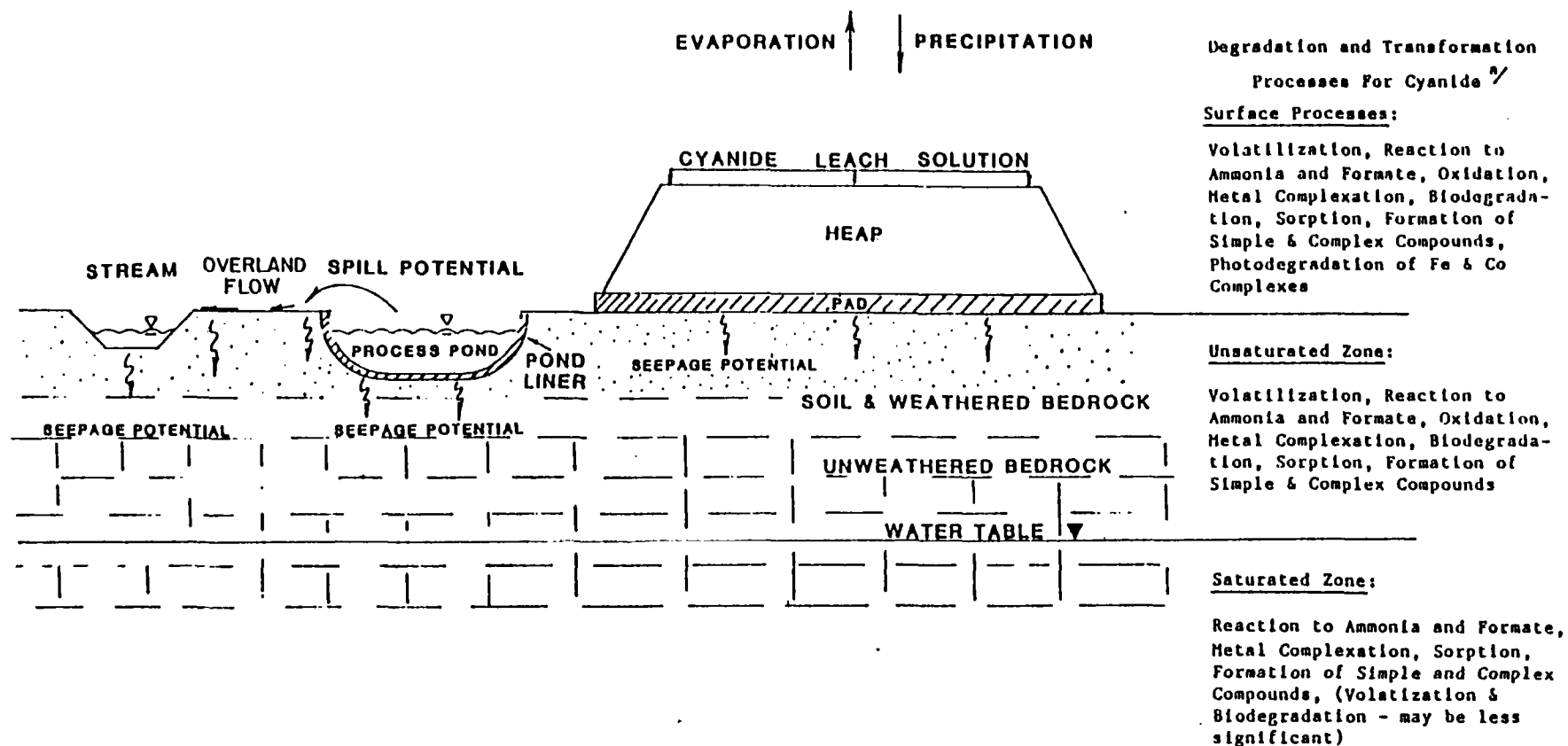
Mobility - PGDN is essentially immiscible with water, but soluble in organic solvents, such as acetone or methanol. Once absorbed in the soil, it can be mobilized only by erosion of the host soil particles. It is not volatile, hence the principal pathways for exposure are by dermal contact or by ingestion.

Toxicity - PGDN is known to have toxic effects on humans; low level acute occupational exposure affecting the nervous system has been discussed in the U.S. Navy Manual [2]. Its toxicity can be estimated, based on established limits for Nitroglycerin or EDN [3].

Persistence - Otto Fuel II is a mixture of PGDN with non-toxic organic stabilizer compounds. It is considered to have a useful shelf life exceeding two years in storage at ambient conditions.

FIGURE 20

SUMMARY OF POTENTIAL DEGRADATION AND TRANSFORMATION  
PROCESSES FOR CYANIDE AT A TYPICAL HEAP LEACH MINING OPERATION



<sup>a/</sup>IF SULFIDE PRESENT:FORMATION OF THIOCYANATE

Concentrations (detectable only in the top 1 ft of sample cores) -  
approximately 300 ft<sup>2</sup> area near the former discharge pipe site:

average of all detectable concentrations = 1900 mg/kg  
maximum concentration observed = 4900 mg/kg

in the runoff stream sediments:

average of the two isolated samples with  
detectable concentrations = 160 mg/kg  
maximum concentration observed = 240 mg/kg

Cyanides, which are present as a result of incomplete combustion of Otto Fuel in torpedo testing, are characterized as follows:

Mobility - Cyanides, being generally soluble in water, are capable of leaching either into surface runoff or into ground water flow. Cyanide concentrations of 0.24 to 1.2 mg/L were observed in the actual runoff stream flow.

Toxicity - Cyanides are notorious for toxicity to humans and animals, due to interference with oxygen metabolism.

Persistence - Cyanides do degrade in the environment. Under acidic conditions, cyanides are converted to the volatile hydrocyanic acid (HCN) and released to the atmosphere. Other mechanisms of cyanide degradation, including ultraviolet light, bacterial action, and direct uptake by plants are known to occur [4].

Concentrations in the top 1 ft of sample cores) - (note that detectable, but generally much smaller concentrations are present further below the soil surface)

approximately 1,000 ft<sup>2</sup> area near the former discharge pipe:  
average of all detectable concentrations = 10 mg/kg  
maximum concentration observed = 54 mg/kg

in the runoff stream sediments:

average of all detectable concentrations	= 6 mg/kg
maximum concentration observed	= 18 mg/kg

in a belt of detectable, but low cyanide concentrations encircling Building 49, at distances of 75 to 300 ft:

average of all detectable concentrations	= 1 mg/kg
maximum concentration observed	= 4 mg/kg

STEP 2: Estimation of Exposure Point Concentrations - Table C-1 summarizes a qualitative exposure pathway analysis for the (existing conditions) baseline case, which reviews the sources and the potential mechanisms for chemical releases. The sources in this case are soils and sediments containing the chemical residues from torpedo test wastewater discharges. The mechanisms for release from these sources include volatilization and fugitive dust emission into air, leaching and erosion into surface water, leaching into ground water, and dermal contact. The qualitative exposure pathway analysis then considers the human populations that may be affected.

In a reasonable worst case scenario, land use following Closure of the Building 49 discharge areas could become residential. Adults and children residing near the site would be chronically exposed by chemical inhalation of volatilized air emissions. The children could be exposed further by episodic ingestion of surface water and/or soil, as well as by direct dermal contact with the soil. Other exposures are possible, but very unlikely. Given the short length (120 ft.) and small size of the runoff stream and its episodic flows following rainfall or snow melt, adult ingestion of surface water would be in that category. Similarly, exposure to PGDN and cyanides would be possible via ingestion of ground water, but not likely, since the shallow ground water aquifer is not suitable for water supply, and there are no known water well users in the vicinity.

Episodic exposures may occur for residents of the metropolitan area (including adults and children residing near the Building 49 discharge area site), via ingestion of small game fowl and/or fish contaminated with cyanides and/or PGDN from Building 49. In the first case, ducks or geese that browsed for food in the former discharge area south of Building 49

would have been exposed to PGDN and/or cyanides by the same pathways that affect the human residents. In the latter case, the fish would have been contaminated in Lake Erie near-shore waters by exposure to sediments containing PGDN and cyanides. (Soluble cyanides transported with the runoff stream would have at least thousand-fold dilution with runoff from other areas served by the TAPCO site storm sewer system. The runoff stream drainage area is estimated to be about 0.1 acre, including the approximately 600 ft<sup>2</sup> affected area, out of about 200 acres total for the TAPCO property.)

Table C-2 summarizes the estimated exposure point concentrations and lists the Applicable or Relevant and Appropriate Requirements (ARARs). The only complete pathway having an ARAR value available for comparison is for ingestion of cyanides from surface water, where the water quality limit of 0.2 mg/L is assumed to apply. The exposure point concentrations of 0.24 to 1.2 mg/L, which were observed in the runoff stream, exceed this ARAR, indicating risk for the children who ingest that water. Soluble PGDN concentrations would be negligible, since it is water-immiscible. Concentrations of PGDN in the runoff stream in particulate form (droplets or soil particles) were also assumed to be negligible, due to the episodic nature of the erosion process. However, the same children would be exposed to direct dermal absorption of PGDN by contact with contaminated soil and sediments.

Table C-3 summarizes the calculations of exposure point concentrations for inhalation by volatilization and subsequent dispersion in air. The volatilization of cyanide and PGDN was estimated, based on mass transfer rate coefficients which were used in a risk assessment on mineral leaching residues [5]. The estimates are for a worst case scenario, based on the coefficients for volatilization from shallow (1 inch depth) quiescent surface waters, at conditions of ambient temperatures and neutral or acidic pH. Dispersion in air was then estimated for a downwind distance of 50 ft (15 m), using a documented model [5]. Exposures due to the belt of detectable, but low cyanide concentrations are seen to be small compared to those from the former discharge area. In the absence of an ARAR value for this exposure pathway of PGDN, Table C-2 lists the occupational health standard for PGDN's close relatives, Nitroglycerin and EDN.

The exposure point concentration for direct dermal contact are the observed 80 to 4900 mg/kg of PGDN and 1 to 54 mg/kg of cyanides range in surface soils and sediments near the former discharge pipe from Building 49.

The exposure point concentrations for ingestion of contaminated game fowl or fish were estimated assuming that ingestion of, or dermal contact with, soil containing PGDN and cyanide results in concentrations in edible tissue reduced by 1:1000 from soil concentrations. This factor is equivalent to daily intake for children and assumes no retention in the tissue.

In a situation such as this, where one or more of the indicator chemicals does not have an ARAR value available, it is necessary to continue with the remaining steps of the Risk Assessment Procedure. Since no values have been established for acceptable intakes (AIC or AIS) for PGDN ingestion and for dermal contact with cyanide or PGDN, the formal Estimation of Chemical Intakes, the Toxicity Assessments and the Risk Characterization steps are partially based on assumed toxicologically conservative values of acceptable intake and must be regarded as semi-quantitative.

STEP 3: Estimation of Chemical Intake is summarized in Table C-4 for PGDN and cyanides. The calculations for exposed adults and children are based on documented reasonable worst case scenario human intake factors for inhalation and ingestion [7]. The exposure factors for dermal contact were estimated for 1 contact event/day resulting in 3 mg soil adherence/sq cm exposed skin area [6]. The ingestion and dermal contact intakes, although episodic, could take place simultaneously and would be additive to the chronic inhalation intake. On a body weight basis, the intakes by children are more significant than those for adults.

STEPS 4 and 5: Toxicity Assessment and Risk Characterization are summarized in Table C-5, which compares the calculated intakes with acceptable intakes. Cyanide intake by children is seen to have a Hazard Index value exceeding 100 percent, confirming the earlier judgement based on exposure point concentrations exceeding the ARAR. In the absence of documented Acceptable Intake values for PGDN, hazard index values were not calculated. The principal intake routes for both PGDN and cyanides are seen to be ingestion of soil and dermal contact.

### 3. RISK ASSESSMENT FOR REMEDIAL ALTERNATIVES

#### 3.1 Risk Assessment Procedure for Remedial Alternatives

Remedial Alternatives can be classified as either source control or management of migration. Source control remedial actions reduce the amount of mobile contaminant present in the soil, before it has migrated much

TABLE C-1  
(continued)

QUALITATIVE ANALYSIS OF EXPOSURE PATHWAYS

Pathway completion:

Possible, but highly unlikely, due to episodic time frame  
and isolated individual particles

Ground Water (shallow aquifer)

Mechanism: Leaching

Release Time Frame: chronic

Release amounts:

PGDN - none: not miscible with water

Cyanide - low, based on concentrations below the detection limit  
observed in the ground water monitoring wells and  
detectable, but low concentrations found in subsurface  
soil samples below 1 ft.

Primary Exposure Points:

Drinking water well users downgradient from the site

Exposure Routes: Ingestion and Dermal Absorption

Number of Persons Potentially Exposed:

Very few: the shallow ground water aquifer is not  
suitable as a water supply for any significant use.

Domestic water supplies in the area use Lake Erie water.

Pathway Completion: Possible, but highly unlikely.

Soils and Sediments containing PGDN and/or Cyanides

Mechanism: Ingestion

Release Time Frame: episodic

Release amounts:

PGDN - low

Cyanide - low

Primary Exposure Points:

Children in the discharge area:

Exposure Routes: Ingestion

Pathway Completion: Possible

Mechanism: Dermal Contact

Release Time Frame: episodic

Release amounts:

PGDN - low

Cyanide - low

Primary Exposure Points:

Children in the discharge area:

Exposure Routes: Dermal Absorption

Pathway Completion: Possible

Mechanism: Ingestion (Indirect)

Release Time Frame: episodic

Release amounts:

PGDN - low

Cyanide - negligible



Table C-2

BASELINE EXPOSURE POINT CONCENTRATIONS (EPCs) AND  
APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS (ARARs)

Pathways	Cyanides	PGDN
Air/Volatilization/Inhalation		
EPC, mg/m <sup>3</sup> (a)	0.0042	0.084
ARAR, mg/m <sup>3</sup>	0.070 (b)	0.048 (c)
Water/Leaching/Ingestion		
EPC, mg/L	1.2	not applicable
ARAR, mg/L	0.2 (d)	n/a (e)
Soil/Ingestion		
EPC, mg/kg	54	4,900
ARAR, mg/kg	20 (b)	n/a
Soil/Animal Contact/Ingestion		
EPC, mg/kg	0.054	4.9
ARAR, mg/kg	n/a	n/a
Soil/Dermal Contact		
EPC, mg/kg	54	4,900
ARAR, mg/kg	20 (b)	n/a

-----  
(a) Table C-3. calculation for atmospheric stability class E

(b) Preliminary target concentration for clean closure [7]

(c) 2 mg/m<sup>3</sup> occupational health standard [3] divided by 42

(d) Drinking Water Standard [1]

(e) no ARAR value currently available [1]

TABLE C-4

## CALCULATION OF BASELINE HUMAN INTAKES

Inhalation		
20 cu m/day	70 kg adult	0.29 cu m/kg/d-adult
10 cu m/day	17 kg child	0.59 cu m/kg/d-child
Exposure Point Conc.		
0.0042 mg/cu m	Cyanides	0.084 mg/cu m PGDN
Intake		
0.0012 mg/kg/day-adult		0.02 mg/kg/day-adult
0.0025 mg/kg/day-child		0.05 mg/kg/day-child
Ingestion from surface water or ground water		
2.0 L/day	70 kg adult	0.029 L/kg/day-adult
0.5 L/day	17 kg child	0.029 L/kg/day-child
Exposure Point Conc.		
1.2 mg/L	Cyanides	not applicable PGDN
Intake		
0.034 mg/kg/day-adult		0.00 mg/kg/day-adult
0.035 mg/kg/day-child		0.00 mg/kg/day-child
Ingestion from soil and sediments		
0.000 kg/day	70 kg adult	0.0E+00 kg/kg/day-adult
0.001 kg/day	17 kg child	5.9E-05 kg/kg/day-child
Exposure Point Conc.		
54 mg/kg	Cyanides	4900 mg/kg PGDN
Intake		
0.000 mg/kg/day-adult		0.00 mg/kg/day-adult
0.000 mg/kg/day-child		0.29 mg/kg/day-child
Ingestion of Contaminated Game Fowl or Fish		
0.50 kg/day	70 kg adult	0.007 kg/kg/day-adult
0.25 kg/day	17 kg child	0.015 kg/kg/day-child
Exposure Point Conc.		
0.054 mg/kg	Cyanides	4.9 mg/kg PGDN
Intake		
0.0004 mg/kg/day-adult		0.035 mg/kg/day-adult
0.0008 mg/kg/day-child		0.072 mg/kg/day-child
Dermal Contact with Contaminated Soil and/or Sediments		
0.000 kg/day	70 kg adult	0.000 kg/kg/day-adult
0.001 kg/day	17 kg child	0.003 kg/kg/day-child
Exposure Point Conc.		
54 mg/kg	Cyanides	4900 mg/kg PGDN
Intake		
0.00 mg/kg/day-adult		0.0 mg/kg/day-adult
0.16 mg/kg/day-child		15 mg/kg/day-child

Table C-5

## BASELINE RISK CHARACTERIZATION

	Cyanides	PGDN
<b>Adults</b>		
Inhalation Intake, mg/kg/day	0.0012	0.02
AIC, mg/kg/day	0.02 (a)	n/a (b)
Hazard Index		6%
Ingestion Intake, mg/kg/day		
Surface water/ground water	0.0343	0.000
Soil & sediments	0.0000	0.000
Contaminated fish/fowl	0.0004	0.035
Total	0.0347	0.035
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index		173%
Dermal Intake, mg/kg/day	0.0000	0.000
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index		0%
=====		
Sum of Hazard Index Values		179%
(b)		
<b>Children</b>		
Inhalation Intake, mg/kg/day	0.0025	0.05
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index		12%
Ingestion Intake, mg/kg/day		
Surface water	0.035	0.00
Soil & sediments	0.003	0.29
Contaminated fish/fowl	0.001	0.07
Total	0.039	0.36
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index		196%
Dermal Intake, mg/kg/day	0.2	15
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index		810%
=====		
Sum of Hazard Index Values		1019%

(a) Reference Dose Value (RfD) (1)

(b) no AIC value available

Table C-6

PROPOSED EXPOSURE POINT CONCENTRATIONS (EPCs) AND  
APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS (ARARs)

Pathways	Cyanides	PGDN
Air/Volatilization/Inhalation		
EPC, mg/m <sup>3</sup>	0.0003 (a) not applicable	
ARAR, mg/m <sup>3</sup>	0.07 (b)	n/a (c)
Water/Leaching/Ingestion		
EPC, mg/L	0.1 (a) not applicable	
ARAR, mg/L	0.2 (d)	n/a
Soil/Ingestion		
EPC, mg/kg,	4 (a) not applicable	
ARAR, mg/kg	20 (b)	n/a
Soil/Animal Contact/Ingestion		
EPC, mg/kg	0.004 (a) not applicable	
ARAR, mg/kg	n/a	n/a
Soil/Dermal Contact		
EPC, mg/kg	4 (a) not applicable	
ARAR, mg/kg	20 (b)	n/a

-----  
(a) EPC values for Cyanides from Table C-2, reduced by 92%

(b) Preliminary target concentration for clean closure [7]

(c) no ARAR value currently available [1]

(d) Drinking Water Standard [1]

TABLE C-7

## CALCULATION OF HUMAN INTAKES FOR PROPOSED REMEDIAL ACTION

Inhalation			
20 cu m/day	70 kg adult		0.29 cu m/kg/d-adult
10 cu m/day	17 kg child		0.59 cu m/kg/d-child
Exposure Point Conc.			
0.0003 mg/cu m	Cyanides	not applicable	PGDN
Intake			
0.0001 mg/kg/day-adult		0.00 mg/kg/day-adult	
0.0002 mg/kg/day-child		0.00 mg/kg/day-child	
Ingestion from surface water or ground water			
2.0 L/day	70 kg adult		0.029 L/kg/day-adult
0.5 L/day	17 kg child		0.029 L/kg/day-child
Exposure Point Conc.			
0.1 mg/L	Cyanides	not applicable	PGDN
Intake			
0.003 mg/kg/day-adult		0.00 mg/kg/day-adult	
0.003 mg/kg/day-child		0.00 mg/kg/day-child	
Ingestion from soil and sediments			
0.000 kg/day	70 kg adult		0.0E+00 kg/kg/day-adult
0.001 kg/day	17 kg child		5.9E-05 kg/kg/day-child
Exposure Point Conc.			
4 mg/kg	Cyanides	not applicable	PGDN
Intake			
0.000 mg/kg/day-adult		0.00 mg/kg/day-adult	
0.000 mg/kg/day-child		0.00 mg/kg/day-child	
Ingestion of Contaminated Game Fowl or Fish			
0.50 kg/day	70 kg adult		0.007 kg/kg/day-adult
0.25 kg/day	17 kg child		0.015 kg/kg/day-child
Exposure Point Conc.			
0.004 mg/kg	Cyanides	not applicable	PGDN
Intake			
0.0000 mg/kg/day-adult		0.000 mg/kg/day-adult	
0.0001 mg/kg/day-child		0.000 mg/kg/day-child	
Dermal Contact with Contaminated Soil and/or Sediments			
0.000 kg/day	70 kg adult		0.000 kg/kg/day-adult
0.051 kg/day	17 kg child		0.003 kg/kg/day-child
Exposure Point Conc.			
4 mg/kg	Cyanides	not applicable	PGDN
Intake			
0.000 mg/kg/day-adult		0.0 mg/kg/day-adult	
0.013 mg/kg/day-child		0 mg/kg/day-child	

Table C-8

## RISK CHARACTERIZATION FOR PROPOSED REMEDIAL ACTION

	Cyanides	PGDN
<b>Adults</b>		
Inhalation Intake, mg/kg/day	0.0001	not applicable
AIC, mg/kg/day	0.02 (a)	n/a (b)
Hazard Index		0.5%
Ingestion Intake, mg/kg/day		not applicable
Surface water/ground water	0.00274	
Soil & sediments	0.00000	
Contaminated fish/fowl	0.00003	
Total	0.00277	
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index		13.9%
Dermal Intake, mg/kg/day	0.0000	not applicable
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index		0.0%
Sum of Hazard Index Values		=====
		14.3% not applicable
		n/a
<b>Children</b>		
Inhalation Intake, mg/kg/day	0.0002	
AIC, mg/kg/day	0.02 (a)	not applicable
Hazard Index		1%
Ingestion Intake, mg/kg/day		
Surface water	0.003	
Soil & sediments	0.000	
Contaminated fish/fowl	0.000	n/a
Total	0.003	
AIC, mg/kg/day	0.02 (a)	not applicable
Hazard Index		16% n/a
Dermal Intake, mg/kg/day	0.013	
AIC, mg/kg/day	0.02 (a)	
Hazard Index		65%
Sum of Hazard Index Values		=====
		82%

-- (a) Reference Dose Value (RfD) [1]

(b) no AIC value available

about 10 ft south of the soil to be excavated, for access by the heavy equipment which otherwise may be mired in the soil after rains. This activity can start as soon as possible, weather permitting. Once started, it will take about two work weeks (14 calendar days) to complete, allowing for possible delays due to adverse weather.

6.5 Excavation of Contaminated Soil from the Building 49 Spill Area will require a Gradall or Clamshell. Soil will be excavated from the approximately 625 sq.ft. polygon area shown in Figure 2.5, to a depth of 1 ft below the interface of competent clay. Sections through the polygon area are shown in Figures 6.5 and 6.6. Assuming that the excavation averages about 4 ft depth, it will amount to about 95 cu.yd. This activity can begin immediately after completion of the roadway, and will take about one work week, weather permitting. As soon as the excavation has been completed, soil sampling can begin (See Subsection 6.9).

6.6 Dredging of the Runoff Stream will also require the Gradall or Clamshell unit. Sediments will be removed from the approximately 120 ft length of the stream, to a depth of 2 ft. A profile section along the stream is shown in Figure 6.7. Assuming a bucket width of 2 ft, the sediments removed would amount to about 18 cu.yd. An additional 1.4 cu.yd. of sediments will be removed from the first culvert (at the south end of the runoff stream) by hand shoveling. Organic debris previously removed from the runoff stream and dumped in the wooded area (Sample Station 11) will be added to the sediments and debris now removed. The dredging will also include removal of sediments from Manhole #7 in the runoff collection system (See Building 49 Study Report, Section 4.2). The dredging can begin after completion of the excavation of contaminated soil, and will take about one work week, weather permitting. Soil sampling can begin along the runoff stream bed as soon as the sediment dredging activity has been completed (See Subsection 6.9).

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6.7 Off-Site Disposal of the Soil and Sediments. The two preceding activities will generate about 130 cu.yd. of soil and sediments, assuming about 10% expansion. This material will be transferred to containers, covered with plastic sheets to keep out rainwater and hauled off-site for disposal by incineration. (In the event that an alternative treatment technology becomes available before approval of the Closure Plan, TRW will investigate its feasibility.) A 25 ft.x 25 ft. container staging area to the north of Building 49 will be protected from contamination by a 20 mil plastic sheet. This activity will follow the soil and sediment removal, as quickly as practicable. Upon completion of this activity, the plastic sheet will be inspected for damage, to determine whether soil sampling would be required.

6.8 Removal and Decontamination of the 1,000 Gallon Underground Separator Tank, the Three Overflow Holding Tanks and Auxiliary Piping can occur at any time following the excavation of contaminated soil. The auxiliary piping will be removed first, about 40 ft. of 6" VT pipe from the former discharge area to the separator tank outlet, about 10 ft. of 6" VT from the separator tank inlet to the connection with the torpedo test cell drains, and about 60 ft. of 6" VT pipe from the separator tank outlet to the overflow holding tanks. Any free liquid in the tanks will be pumped out and retained for off-site disposal, if necessary, pending analysis for PGDN and total cyanides. The tanks will then be exhumed.

This activity will require a backhoe to unearth the underground facilities, which lie at typical depths up to about 4 ft. It can be completed within two work weeks, weather permitting. Decontamination of the tanks and piping are described in Section 9.

6.9 Soil Sampling at Building 49 and Subsequent Laboratory Analysis of the Soil Samples will begin upon completion of the excavation, removal or demolition activities above. A maximum of five weeks (35 calendar days) will be required for the laboratory results to be reported. A grid sampling strategy, will be followed in the Polygon area to ensure that no contaminated soil remains. The proposed sampling grid and



other details of the soil sampling are discussed in Section 11. Two samples will also be taken at Sample Station 11, at the location where organic debris previously dredged from the runoff stream was stock-piled.

Soil samples will be taken at four locations formerly under the separator tank, four locations under the overflow holding tanks and at 5 ft. intervals along the former piping. Samples also will be taken at all pipe connections and any other locations appearing to have suffered leakage.

A Soil Boring rig will be used to take the soil samples at Building 49. The soil samples will be collected in Shelby Tubes representing 1 ft intervals of depth below the surface (after excavation) down to the bedrock shale.

The Shelby Tubes or cores will be capped, marked with identifying numbers and delivered to a certified laboratory for chemical analysis. Chain-of-Custody documentation and other quality control procedures are discussed in Section 11. The analysis will be only for PGDN and Total Cyanide.

Contingent on the soil sampling results, additional soil removal and/or dredging may be required to ensure that all hazardous waste and contaminated soil have had proper disposal. Soils found to contain higher than 10 mg/kg total cyanides or detectable PGDN will be removed for off-site disposal, pending laboratory analysis results for the soil samples. See Section 11.1 and the Risk Assessment (Attachment 2, the Building 49 Study Report, Appendix C) for details on Soil Sampling and acceptable cyanide levels.

Any equipment used in this task will have to be decontaminated before it can be allowed to leave the site (See Section 6.15).

6.10 Backfilling and Final Grading of the Soil Removal Area will use clean borrow material. Soil from the former shrapnel barrier mound to the south of Building 49 will be used for this. It does not contain detectable concentrations of cyanides, based on analysis of a composite sample which was collected during the preparation of this Closure Plan. This activity can begin after analytical laboratory tests confirm that the remaining soil is free of PGDN (torpedo fuel) and has acceptable cyanide concentrations (not exceeding 10 mg/kg). It can be completed within one work week, weather permitting.

6.11 Removal of Wood Flooring Blocks must precede the other closure activities at the Dock 2-B former TRW Hazardous Waste Storage Area. Wood blocks along the periphery of this area will be sampled, as indicated on Figure 6.2 and analyzed by GC/MS (Method 8240) for the spent solvents that were stored at the Dock, including TCE (trichloroethylene), PCE (tetrachloroethylene), TCA (trichloroethene), MEK (Methyl ethyl ketone), and dioxane (See Table 2.1), to identify wood blocks that may have been contaminated by spills. (Note that operational records indicate no spills.) Any peripheral blocks found to be contaminated will be removed, and additional samples further away from the former TRW area will then be required to define the affected area.

6.12 Decontamination of Concrete Flooring at Dock 2-B and Building 45. The underlying concrete flooring at Dock 2-B will be decontaminated using three pressurized water rinses and scrubbing or scraping at areas showing visible residues. The rinseates will be retained and analyzed for hazardous waste constituents, particularly for the solvents once stored at the dock (including TCE, PCE, TCA, MEK and dioxane) from spill residues that may have penetrated through the blocks. If any hazardous constituent is present at concentrations exceeding clean levels (as noted below) in the third rinseate, samples will be taken of the concrete at the selected areas defined on the 5 ft. grid spacing shown in Figure 6.8 in order to identify the contaminated areas.

The concrete flooring in the Building 45 Target House will be decontaminated using three pressurized water rinses and scrubbing or scraping at areas showing visible residues. The rinseates will be retained and analyzed for hazardous waste constituents, particularly the xylene once stored there, total chromium (once stored there and detected in preliminary tests, Section 5.2) and total lead (residue from pre-RCRA use). If the third rinse contains any hazardous constituents at a concentration exceeding clean levels (as noted below), the concrete will be sampled in order to identify the specific areas contaminated. The samples will be taken by scraping the concrete at the selected areas defined by the 5 ft. grid spacing shown in Figure 6.9, which will extend the sampling to include the sumps and the pits adjoining the Target House on the east and west.

The rinseates will be retained for off-site disposal, pending the laboratory analysis results. Disposal as a RCRA waste will be required for rinseates containing any hazardous waste constituent at concentrations higher than clean levels, which shall be set as follows:

- 1) The public drinking water minimum contaminant level (MCL) for hazardous waste constituents as promulgated in 40 CFR 141.11 and OAC 3745-81-11 for inorganics and 40 CFR 141.12 and OAC 3745-81-12 for organics shall be used as the rinseate clean standard.
- 2) If an MCL is not available, then the maximum contaminant level goal (MCLG) as promulgated in 40 CFR 141.50 shall be used for the clean standard; or
- 3) If neither an MCL or an MCLG is available, 1 mg/l shall be used for the clean standard. If the MCL or MCLG is less than the contaminant's analytical detection limit using methods found in USEPA Publication SW-846, the SW-846 analytical detection limit shall be used as the clean standard.

This activity can start after the wood flooring blocks have been removed. An estimated four weeks (28 calendar days) will be required for the laboratory results to be available.

- 6.13 Contingent Demolition of Concrete Flooring in the Dock 2-B former TRW Hazardous Waste Storage Area and in the Building 45 Target House is a contingent activity, to be carried out at either or both of the locations, only at the specific areas of the concrete flooring identified as containing hazardous waste residues. Level B personnel protection (impervious clothing and supplied air respiration) will be required in Building 45; Level C (air filtration) will suffice at Dock 2-B. A crew of two will work in each area, one operating the hammer and the other assisting with dust control. This activity will take about two weeks (14 calendar days) for a single crew. The dust control water spray will be collected for off-site disposal.

The soil underlying the concrete removed by demolition will be inspected visually for evidence of hazardous waste penetration through the now removed concrete flooring. If necessary, sampling and analysis and subsequent soil removal will be carried out.

All concrete flooring removed by demolition from both Dock 2-B and Building 49 will be replaced by patching. At Dock 2-B, additional concrete will be applied on top of the existing flooring (patched as necessary). This surface will be sealed by coating with coal-tar epoxy, to provide a suitable flooring service for future Argo-Tech use of the area for 90 day storage of hazardous materials.

- 6.14 Off-Site Disposal of Rubble from Dock 2-B and Building 45 will generate an estimated 5 tons of wood blocks, assuming a wood block thickness of 1.5 inches. The concrete demolished in the two buildings is estimated to amount to 20 cu.yd., assuming a concrete thickness of 1 ft and 75% expansion. The rubble will be accumulated at each location in separate covered containers. These activities will follow the demolition as quickly as practicable.

The wood blocks from Dock 2-B will be collected in fibre drums for off-site treatment by incineration, and the resultant ash will then be disposed of by landfilling. The concrete rubble resulting from demolition, if any, would have to be disposed of at a landfill certified for hazardous wastes.

6.15 Decontamination of Equipment Used in the Closure is scheduled upon completion of the activities above. A portable steam generator or a high pressure water sprayer will be set up near the work areas. Enclosures will be set up to collect the condensate or washwater, for off-site disposal (See Section 14). This will ensure that all particles of hazardous waste and/or contaminated soil adhering to the equipment are dislodged and disposed of. Decontamination of the equipment should be done as quickly as possible after the last use of each item.

6.16 Certification is the final task. The independent registered Professional Engineer retained by TRW will have been present on-site during all of the activities enumerated above. Upon completion of all required site work and after review of the soil sampling laboratory data, the Engineer shall submit his report which will certify that all closure activities have been carried out in compliance with the Closure Plan. Further details on Certification are in Section 15.

This activity should have been completed within two weeks (14 days) after completion of the Final Closure field activity.

## 9. DECONTAMINATION EFFORTS

The 1,000 gallon underground separator tank formerly used to treat discharges of wastewater from torpedo testing operations, the vitreous clay auxiliary piping connecting this tank to Building 49 and to the discharge area, and the three underground holding tanks for torpedo testing wastewater will be unearthed and removed. These items will be taken to Building 48, the former laundry facility for the torpedo test complex, to be washed with a detergent solution (Wisk) and rinsed with city water. The detergent is routinely used for cleaning residues of torpedo fuel during torpedo test operations. This washing and rinsing will be repeated as necessary until the intensely reddish torpedo fuel color is no longer visible. The wash water and rinseate will be collected and disposed of off-site. See Figure 6.4 for layout of closure activities near Building 49.

Decontamination of concrete flooring under Dock 2B and at Building 45 will use three sequential rinses with pressurized water, and scrubbing or scraping, if possible residuals are detected. The rinseates will be retained for off-site disposal and analyzed for volatile solvents (Method 8240) and EP Toxicity Metals (See Section 6.12).

Clean levels for rinseates from decontamination of the 1,000 gallon storage tank and appurtenant piping located at Building 49, and the concrete flooring in the Dock 2-B and Building 45 areas shall be set as follows:

- 1) The public drinking water minimum contaminant level (MCL) for hazardous waste constituents as promulgated in 40 CFR 141.11 and OAC 3745-81-11 for inorganics and 40 CFR 141.12 and OAC 3745-81-12 for organics shall be used as the rinseate clean standard.
- 2) If an MCL is not available, then the maximum contaminant level goal (MCLG) as promulgated in 40 CFR 141.50 shall be used for the clean standard; or
- 3) If neither an MCL or an MCLG is available, 1 mg/l shall be used for the clean standard. If the MCL or MCLG is less than the contaminant's analytical detection limit using methods found in USEPA Publication SW-846, the SW-846 analytical detection limit shall be used as the clean standard.

Decontamination of equipment used in the Closure activities is discussed in Section 14.

- o The 625 sq.ft. irregular polygon area for soil removal at the former torpedo test wastewater discharge area: 7 cells/29 (Figure 11.1).
- o The 120 ft long runoff stream channel: 6 cells/24 (Figure 11.2).

In addition, two soil samples will be taken at Sample Location 11, where organic debris (previously dredged from the runoff stream) was stockpiled. See the Building 49 Study Report, Section 4.2.

The soil exposed after removal of the 1,000 gallon separator tank and an estimated 40 ft. of auxiliary piping should be sampled at four locations previously under the tank and at piping connections, if possible, and at sample points spaced about 5 ft.

If necessary (because of damage to the 20 mil plastic sheet), the 25 ft. x 25 ft. container staging area will be sampled using a 7 ft interval grid.

11.1.4 Sampling Methods and Equipment. A Soil Boring rig will be used to take the soil samples near Building 49. The samples will be collected in Shelby Tubes representing 1 ft intervals of depth below the surface. The tubes will be capped, marked with identifying numbers and delivered to a certified laboratory for chemical analysis.

#### 11.2 Plan for Soil Sampling at Dock 2-B and Building 45, If Required

Concrete flooring will be demolished in Building 45 at the specific locations found to contain hazardous waste residues (See Section 6.12). It may also be necessary to demolish the concrete sub-flooring at Dock 2-B, at any specific locations found to contain hazardous waste residues. The surface soils immediately beneath the affected concrete will be inspected and, if necessary, sampled to ensure that no hazardous waste residues remain.

This contingent soil sampling will be limited to the specific parameters which were identified in the analysis of the concrete samples. These soil core samples, if any, will be taken by manually driving 2 inch pipes using a sledge hammer. The test methods for analyzing the parameters

will be those provided in U.S. EPA Manual SW-846. Section 10, Criteria for Soil Contamination, presents the rationale for establishing what shall be taken to constitute a "clean" level for soil at the site.

### 11.3 Background Samples

Additional soil sampling will be undertaken by TRW, not later than the beginning of closure activities, to provide a data base of four (4) or more soil samples taken at unaffected locations within the TAPCO site.

### 11.4 Quality Assurance/Quality Control Plan

The soil and sediment sampling plan will include 10% blind duplicates and field blanks, which will be submitted for laboratory analysis along with the regular samples. All sample numbers will be assigned using a sequential code, except for duplicates and blanks, which will be identified as such. Permanent numbered gummed labels and Chain-of-Custody Forms will be provided.

TRW's laboratory services subcontractor will be required to submit details of its analytical Quality Assurance program. This must include procedures for sample acceptance and logging in, quality control (QC) sampling of at least 10 percent (10%) of all logged samples (excepting field blanks and duplicates) for lab duplicate or spike tests. Spike tests shall include matrix spikes and, for GC/MS tests, surrogate spikes. Relative percent deviations for duplicates and spike recoveries shall be reported for all lab QC samples. In addition, laboratory documentation measures will be required to ensure the integrity and legal validity of all analytical results.



in the runoff stream sediments:

average of all detectable concentrations	= 6 mg/kg
maximum concentration observed	= 18 mg/kg

in a belt of detectable, but low cyanide concentrations encircling Building 49, at distances of 75 to 300 ft:

average of all detectable concentrations	= 1 mg/kg
maximum concentration observed	= 4 mg/kg

STEP 2: Estimation of Exposure Point Concentrations - Table C-1 summarizes a qualitative exposure pathway analysis for the (existing conditions) baseline case, which reviews the sources and the potential mechanisms for chemical releases. The sources in this case are soils and sediments containing the chemical residues from torpedo test wastewater discharges. The mechanisms for release from these sources include volatilization and fugitive dust emission into air, leaching and erosion into surface water, leaching into ground water, and dermal contact. The qualitative exposure pathway analysis then considers the human populations that may be affected.

In a reasonable worst case scenario, land use following Closure of the Building 49 discharge areas, could become residential. Adults and children residing near the site would be chronically exposed by chemical inhalation of volatilized air emissions. The children could be exposed further by episodic ingestion of surface water and/or soil, as well as by direct dermal contact with the soil. Given the short length (120 ft.) and small size of the runoff stream and its episodic flows following rainfall or snow melt, adult ingestion of surface water would not be reasonable. No significant adult or child exposure to PGDN and cyanides seems possible via ingestion of ground water. The shallow ground water aquifer is not suitable for water supply, and there are no known water well users in the vicinity.

Additional episodic exposures may occur for the same population of adults and children residing near the Building 49 discharge area site (as well as many others). These exposures would be via ingestion of small game fowl and/or fish contaminated with cyanides and/or PGDN from Building 49. In the former case, ducks or geese that browsed for food in the former

discharge area south of Building 49 would have been exposed to PGDN and/or cyanides by the same pathways that affect the human residents. In the latter case, the fish would have been contaminated in Lake Erie near-shore waters by exposure to sediments containing PGDN and cyanides. (Soluble cyanides transported with the runoff stream would have at least thousand-fold dilution with runoff from other areas served by the TAPCO site storm sewer system. The runoff stream drainage area is estimated to be about 0.1 acre, including the approximately 600 ft<sup>2</sup> affected area, out of about 200 acres total for the TAPCO property.)

Table C-2 summarizes the estimated exposure point concentrations and lists the Applicable or Relevant and Appropriate Requirements (ARARs). The only complete pathway having an ARAR value available for comparison is for ingestion of cyanides from surface water, where the water quality limit of 0.2 mg/L is assumed to apply. The exposure point concentrations of 0.24 to 1.2 mg/L, which were observed in the runoff stream, exceed this ARAR, indicating risk for the children who ingest that water. Soluble PGDN concentrations would be negligible, since it is water-immiscible. Concentrations of PGDN in the runoff stream in particulate form (droplets or soil particles) were also assumed to be negligible, due to the episodic nature of the erosion process. However, the same children would be exposed to direct dermal absorption of PGDN by contact with contaminated soil and sediments.

Table C-3 summarizes the calculations of exposure point concentrations for inhalation by volatilization and subsequent dispersion in air. The volatilization of cyanide and PGDN was estimated, based on mass transfer rate coefficients which were used in a risk assessment on mineral leaching residues [5]. The estimates are for a worst case scenario, based on the coefficients for volatilization from shallow (1 inch depth) quiescent surface waters, at conditions of ambient temperatures and neutral or acidic pH. Dispersion in air was then estimated for a downwind distance of 50 ft (15 m), using a documented model [6]. Exposures due to the belt of detectable, but low cyanide concentrations are seen to be small compared to those from the former discharge area.

The exposure point concentration for direct dermal contact with PGDN is the observed 80 to 4900 mg/kg range in surface soils near the former discharge pipe from Building 49. In the absence of an ARAR value for this

exposure pathway of PGDN, Table C-2 lists the occupational health standard for PGDN's close relatives, Nitroglycerin and EDN.

The exposure point concentrations for ingestion of contaminated game fowl or fish were estimated assuming that an animal ingested 1 gram of contaminated soil and the PGDN and cyanide in that soil are retained in 1 kg of edible tissue, i.e., a dilution of 1:1000 from soil concentrations.

In a situation such as this, where one or more of the indicator chemicals does not have an ARAR value available, it is necessary to continue with the remaining steps of the Risk Assessment Procedure. Since no values have been established for acceptable intakes (AIC or AIS) for PGDN ingestion and for dermal contact with cyanide or PGDN, the formal Estimation of Chemical Intakes, the Toxicity Assessments and the Risk Characterization steps are partially based on assumed toxicologically conservative values of acceptable intake and must be regarded as semi-quantitative.

STEP 3: Estimation of Chemical Intake is summarized in Table C-4 for PGDN and cyanides. The calculations for exposed adults and children are based on reasonable worst case scenario human exposure factors for inhalation, ingestion and dermal contact. The ingestion and dermal contact intakes, although episodic, could take place simultaneously and would be additive to the chronic inhalation intake. On a body weight basis, the intakes by children are more significant than those for adults.

STEPS 4 and 5: Toxicity Assessment and Risk Characterization are summarized in Table C-5, which compares the calculated intakes with acceptable intakes. Cyanide ingestion by children is seen to have a Hazard Index value exceeding 100 percent, confirming the earlier judgement based on exposure point concentrations exceeding the ARAR. Ingestion of surface water is the most significant intake route for this. In the absence of documented Acceptable Intake values for PGDN, hazard index values were not calculated. The principal PGDN intake routes are seen to be ingestion of soil and dermal contact.

### 3. RISK ASSESSMENT FOR REMEDIAL ALTERNATIVES

#### 3.1 Risk Assessment Procedure for Remedial Alternatives

Remedial Alternatives can be classified as either source control or management of migration. Source control remedial actions reduce the amount of mobile contaminant present in the soil, before it has migrated much

beyond the initial discharge area, e.g., by excavation or by immobilization. Management of migration alternatives would address contaminants that have migrated away from the source to reduce the exposure point concentrations, e.g., by treating ground water or runoff. Whichever type of alternative is considered, the objective is to reduce the risk level for exposure point populations to be within an acceptable target risk range.

For non-carcinogens, an ARAR provides a specific target exposure point concentration as a performance goal for each indicator chemical. If no ARAR value is available, the intakes in mg/kg body weight for exposure point populations should be reduced to acceptable levels (AIC or AIS). For carcinogenic indicator chemicals, remedies must reduce exposure point chemical concentrations to levels associated with a carcinogenic risk range of  $10^{-4}$  to  $10^{-8}$ .

In general, the concentration of chemical residues in soil required to achieve the desired exposure point concentration for a given alternative is not known in advance. Thus, evaluation of alternatives follows a tiered approach, as follows:

- 1) Reassess the indicator chemicals to determine whether any additions are necessary (usually required only for management of migration alternatives, in the event that an indicator chemical; used for the baseline study is not treatable).
- 2) Determine exposure pathways for each alternative, if different from the baseline study (usually required only for management of migration alternatives).
- 3) Develop preliminary target concentrations, based either on ARAR or potential carcinogenic indicator chemicals. (Carcinogens usually drive the final design.)
- 4) If no ARARs are available for the non-carcinogenic indicator chemicals, estimate the long-term concentrations to ensure that acceptable risk levels (chronic hazard index) are attained.
- 5) Estimate the target release rates, i.e., back calculate release rates which would result in target concentrations at the exposure points. Repeat Steps 1 through 4, if necessary.
- 6) Assess potential short-term health effects of remedial alternatives, including subchronic exposures, management practices during

remediation, and any potential effects that might result from failure.

### 3.2 Remedial Alternatives for the Former Building 49 Spill Area

The remedial actions considered for the Building 49 torpedo test wastewater discharge area were source control alternatives. Although PGDN and cyanides have migrated away from the former discharge area due to erosion, only isolated locations in the runoff stream have been affected. The situation does not require management of migration alternatives.

It is Engineering-Science's (ES) opinion that no alternative can be considered acceptable, if it leaves the chemical residues near Building 49 unchanged. The cyanide concentrations may eventually decrease to acceptable levels due to chemical degradation, volatilization, bacterial action, plant uptake or leaching. However, in the absence of some remedial action, the threats to future resident populations discussed in the preceding section would abate very slowly.

It is recommended to undertake a remedial action to remove soil from the area of highest chemical residue concentrations, for appropriate disposal off site and with due precautions to avoid mobilization of PGDN or cyanide during removal (See Figures 5 & 6 in the Building 49 Study Report text and Appended Drawing 7). This would result in excavation of soil from an irregular polygon area (about 625 ft<sup>2</sup>) around the former discharge pipe and dredging of the entire length of the runoff stream (about 120 ft). All soils containing detectable PGDN and/or cyanides at concentrations exceeding 10 mg/kg would be removed. However, soil outside of these areas containing cyanide at concentrations below 10 mg/kg would remain undisturbed. This is more stringent than the preliminary target concentration value of 20 mg/kg for cyanides in soil established in the U.S. Environmental Protection Agency guidance for "Clean Closures" [7].

Alternatives which would not involve removal of soil and sediments for treatment and disposal (i.e., capping the polygon area and regrading to divert both surface runoff and ground water flow from that area) were considered qualitatively. However, any such remedial action would be required to include facilities for monitoring and control of any leachate and/or post-closure ground water quality monitoring for at least 30 years.

### 3.3 Quantitative Risk Assessment for the Recommended Alternative

A formalized risk assessment of the soil excavation for off-site treatment and disposal alternative follows. This risk assessment evaluates the hazards that may result from allowing low concentrations of cyanide, below 10 mg/kg, to remain in the soil on site, based on the rationale that the cyanide concentrations which would leach into surface water or ground water would not pose a risk for public health. A similar rationale was followed in recent actions by State agencies and the USEPA with respect to cyanides in mineral processing residues [5].

STEP 1: Review of Indicator Chemicals is cursory at this stage, since PGDN will have been removed to below detectable concentrations. Only Cyanides will be of concern.

#### Concentrations:

near the former discharge pipe site, cyanides will have been removed to below 10 mg/kg, with the resultant distribution in an approximately 400 ft<sup>2</sup> area as follows:

average of all detectable concentrations = 2 mg/kg  
maximum concentration remaining = 5 mg/kg

in the runoff stream, the entire channel will have been dredged, which will remove all cyanides previously there;

however, the belt of soil encircling Building 49 containing detectable, but low cyanide concentrations, will remain as before:

average of all detectable concentrations = 1 mg/kg  
maximum concentration observed = 4 mg/kg

STEP 2: Estimation of Exposure Point Concentrations is concerned only with Cyanides, and only for the same resident human populations as in the Baseline Assessment. The exposure pathways previously identified for cyanides would remain, but with decreased exposure point concentrations. The exposure point concentration estimates in Table C-6 are based on reductions of the affected area size and its cyanide concentrations. The recommended remedial action will reduce the soil area containing cyanides

to about 40 percent of its original size, and the average of detectable cyanide concentrations would be about 20 percent of the present value. Thus, the amount of cyanides remaining in the former discharge would be about 8 percent of the present quantity. Air emissions and leaching should be reduced by 92 percent.

The target concentration for cyanide at the exposure points are the ARARs value listed in Table C-6, which are based on Preliminary Target Values for Clean Closures [7]. It is seen that the estimated exposure point concentrations of cyanide do not exceed these values, hence, the recommended remedial action would be adequate.

STEPS 3 THROUGH 5: Estimation of Chemical Intakes, Toxicity Assessment and Risk Characterization are summarized in Tables C-7 and C-8. The intake estimates are based on 92 percent reductions of the exposure point concentrations for cyanides from the former discharge area and unabated exposure point concentrations due to the encircling belt of detectable, but low concentrations of cyanides. The resultant hazard index reductions for cyanide ingestion by children to well below 100 percent confirms the projected efficacy of the proposal remedial action.

TABLE C-1

QUALITATIVE ANALYSIS OF EXPOSURE PATHWAYS

Air Emissions

Mechanism: Volatilization from surface soil or ponded surface water

Release Time Frame: chronic

Release amounts:

PGDN - low: vapor pressure =  $0.9 \times 10^{-4}$  atmospheres at 77°F  
for PGDN in pure liquid form

Cyanide - Low, and requires neutral or acidic pH to be mobilized  
for air emission. Estimated vapor pressure of HCN for  
water containing 1 mg/L of cyanide =  $0.7 \times 10^{-6}$   
atmospheres at 77°F

Primary Exposure Points:

Future residents within 500 feet of the site

Exposure Route: Inhalation

Pathway Completion: Possible

Mechanism: Fugitive Dust Generation

Release Time Frame: episodic, at times of high wind

Release amounts: low, due to generally wet environment for soils and  
sediments

Primary Exposure Points:

Future residents within 500 feet of the site

Exposure Route: Inhalation

Pathway Completion: Very unlikely, due to low amounts  
released

Surface Water Runoff (overland flow and ground water flow discharging into  
the runoff stream)

Mechanism: Leaching

Release Time Frame: chronic

Release amounts:

PGDN - none: not miscible with water

Cyanide - low, ranging from 0.01 to 1 gram/day, based on observed  
concentrations and flows

Primary Exposure Points:

Children in the discharge area, drinking from the runoff stream

Exposure Route: Ingestion

Pathway Completion: Possible

Mechanism: Erosion of soil particles

Release Time Frame: episodic, following heavy rainfall

Release amounts: low, only occasional isolated particles have been  
released, based on sampling results for runoff stream  
sediments

Primary Exposure Points:

Residents of the Metropolitan Area:

Exposure Route: Ingestion of fish from Lake Erie near shore  
waters contaminated by sediments transported through the  
runoff stream, the TAPCO Plant storm sewers and the city of  
Euclid storm sewers into Lake Erie.



TABLE C-1  
(continued)

QUALITATIVE ANALYSIS OF EXPOSURE PATHWAYS

Pathway completion:

Possible, but highly unlikely, due to episodic time frame  
and isolated individual particles

Ground Water (shallow aquifer)

Mechanism: Leaching

Release Time Frame: chronic

Release amounts:

PGDN - none: not miscible with water

Cyanide - low, based on concentrations below the detection limit  
observed in the ground water monitoring wells and  
detectable, but low concentrations found in subsurface  
soil samples below 1 ft.

Primary Exposure Points:

Drinking water well users downgradient from the site

Exposure Routes: Ingestion and Dermal Absorption

Number of Persons Potentially Exposed:

None: the shallow ground water aquifer is not suitable  
as a water supply for any significant use. Domestic  
water supplies in the area use Lake Erie water.

Pathway Completion: not complete → not necessary to complete

Soils and Sediments containing PGDN and/or Cyanides

Mechanism: Ingestion

Release Time Frame: episodic

Release amounts:

PGDN - low

Cyanide - negligible

Primary Exposure Points:

Children in the discharge area:

Exposure Routes: Ingestion

Pathway Completion: Possible

Mechanism: Dermal Contact

Release Time Frame: episodic

Release amounts:

PGDN - low

Cyanide - negligible

Primary Exposure Points:

Children in the discharge area:

Exposure Routes: Dermal Absorption

Pathway Completion: Possible

Mechanism: Ingestion and/or Dermal Contact

Release Time Frame: episodic

Release amounts:

PGDN - low

Cyanide - negligible

TABLE C-1  
(continued)

QUALITATIVE ANALYSIS OF EXPOSURE PATHWAYS

Primary Exposure Points:

Residents of the Metropolitan Area:

Exposure Routes: Ingestion of ducks or geese that browsed for  
food in the former discharge area

Pathway Completion: Possible, but highly unlikely

Table C-2

BASELINE EXPOSURE POINT CONCENTRATIONS (EPCs) AND  
APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS (ARARs)

Pathways	Cyanides	PGDN
Air/Volatilization/Inhalation	<sup>1,0042</sup>	
EPC, mg/m3 (a)	0	0 <sup>.084</sup>
ARAR, mg/m3	<sup>107</sup> 0 (b)	0 (c) <sup>.043</sup>
Water/Leaching/Ingestion		
EPC, mg/L	<sup>12</sup> 1	not applicable
ARAR, mg/L	0 (d)	n/a (e)
Soil/Ingestion		
EPC, mg/kg	54	4,900
ARAR, mg/kg	20 (b)	n/a
Soil/Animal Contact/Ingestion		
EPC, mg/kg	<sup>54</sup> or <sup>0.054</sup> 0	5
ARAR, mg/kg	n/a	n/a
Soil/Dermal Contact		
EPC, mg/kg	54	4,900
ARAR, mg/kg	<sup>N/A</sup> 20 (b)	n/a

- 
- (a) Table C-3, calculation for atmospheric stability class E
  - (b) Preliminary target concentration for clean closure [7]
  - (c) 2 mg/m3 occupational health standard [3] divided by 42
  - (d) Drinking Water Standard [1]
  - (e) no ARAR value currently available [1]

Table C-3

Estimation of Exposure Point Concentrations  
 Inhalation of Volatilized Cyanides and PGDN

	Cyanides			PGDN		
Transfer coefficient (quiescent)	0.46 kg/hr/m <sup>2</sup> /(mg/L)			0.016 kg moles/hr/m <sup>2</sup> /a		
Stability Class	F	E	D	F	E	D
Wind velocity, m/s	1.0	2.0	3.0	1.0	2.0	3.0
Transfer coefficient (wind agitated)	0.65	0.80	0.92	0.023	0.028	0.032
Baseline Case	Former Discharge Area					
Maximum Driving Force	1.2 mg/L			9.0E-05 atmosphere		
Transfer Area	92 m <sup>2</sup>			27 m <sup>2</sup>		
Volatilization rate	72	88	102	1430	1751	2022
Distance Downwind (x)	0.015 km			0.015 km		
Sigma y, m (horizontal)	0.7	1.0	1.4	0.7	1.0	1.4
Sigma z, m (vertical)	0.6	0.9	1.2	0.6	0.9	1.2
Conc. at (x), mg/m <sup>3</sup>	0.0155	0.0042	0.0018	0.308	0.084	0.036
Baseline Case	Border Ring Area					
Maximum Driving Force	0.12 mg/L			not applicable		
Transfer Area	100 m <sup>2</sup>					
Volatilization rate	7.8	9.6	11.0			
Distance Downwind (x)	0.015 km					
Sigma y, m (horizontal)	0.7	1.0	1.4			
Sigma z, m (vertical)	0.6	0.9	1.2			
Conc. at (x), mg/m <sup>3</sup>	0.0017	0.0005	0.0002			

Reference: Superfund Exposure Assessment Manual, OSWER Directive 9285.5-1  
 Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response  
 U.S. Environmental Protection Agency, Washington, January, 1986; pp. 4-17 through 4-21

TABLE C-4

## CALCULATION OF BASELINE HUMAN INTAKES

Inhalation		
20 cu m/day	70 kg adult	0.29 cu m/kg/day-adult
10 cu m/day	17 kg child	0.59 cu m/kg/day-child
Exposure Point Conc.		
<del>0.0022</del> mg/cu Cyanides	<sup>.034</sup> 0.069 mg/cu m	PGDN
Intake <sup>.0042</sup>		
<del>0.0006</del> mg/kg/day-adult	<sup>.002</sup> 0.02 mg/kg/day-adult	
<del>0.0013</del> mg/kg/day-child	<sup>.044</sup> 0.04 mg/kg/day-child	
Ingestion from surface water		
<sup>1.0</sup> 0.0 L/day	70 kg adult	<sup>.0029</sup> 0.000 L/kg/day-adult
0.5 L/day	17 kg child	0.029 L/kg/day-child
Exposure Point Conc.		
1.2 mg/L Cyanides	0.00 mg/L	PGDN
Intake <sup>.0035</sup>		
0.000 mg/kg/day-adult	0.00 mg/kg/day-adult	
0.035 mg/kg/day-child	0.00 mg/kg/day-child	
Ingestion from soil and sediments		
0.000 kg/day	70 kg adult	0.0E+00 kg/kg/day-adult
0.001 kg/day	17 kg child	5.9E-05 kg/kg/day-child
Exposure Point Conc.		
<del>240</del> mg/kg Cyanides	4900 mg/kg	PGDN
Intake <sup>.003</sup>		
0.000 mg/kg/day-adult	0.00 mg/kg/day-adult	
<del>0.014</del> mg/kg/day-child	0.29 mg/kg/day-child	
Ingestion of Contaminated Game Fowl or Fish		
0.50 kg/day	70 kg adult	0.007 kg/kg/day-adult
0.25 kg/day	17 kg child	0.015 kg/kg/day-child
Exposure Point Conc.		
0.054 mg/kg Cyanides	4.9 mg/kg	PGDN
Intake		
0.0004 mg/kg/day-adult	0.035 mg/kg/day-adult	
0.0008 mg/kg/day-child	0.072 mg/kg/day-child	
Dermal Contact with Contaminated Soil and/or Sediments		
0.0 kg/day	70 kg adult	0.000 kg/kg/day-adult
1.0 kg/day	17 kg child	0.059 kg/kg/day-child
Exposure Point Conc.		
0.054 mg/kg Cyanides	4.9 mg/kg	PGDN
Intake		
0.0000 mg/kg/day-adult	0.000 mg/kg/day-adult	
0.0032 mg/kg/day-child	0.288 mg/kg/day-child	

Table C-5

## BASELINE RISK CHARACTERIZATION

	Cyanides	PGDN
<b>Adults</b>		
Inhalation Intake, mg/kg/day	<sup>12</sup> 0.0006	0.02
AIC, mg/kg/day	0.02 (a)	n/a (b)
Hazard Index	<sup>3%</sup> 6	
Ingestion Intake, mg/kg/day		
Surface water	<sup>35</sup> 0.0000	0.000
Soil & sediments	0.0000	0.000
Contaminated fish/fowl	0.0004	0.035
Total	<sup>35</sup> 0.0004	0.035
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index	<sup>2%</sup> 127%	
Dermal Intake, mg/kg/day	0.0000	0.000
AIC, mg/kg/day	n/a	n/a
Hazard Index	--	
<b>Children</b>		
Inhalation Intake, mg/kg/day	<sup>0.0013</sup> 0.0013	0.04
AIC, mg/kg/day	0.02 (a)	n/a (b)
Hazard Index	<sup>7%</sup> 12.5%	
Ingestion Intake, mg/kg/day		
Surface water	<sup>0.035</sup> 0.035	0.00
Soil & sediments	0.014	0.29
Contaminated fish/fowl	0.001	0.07
Total	0.050	0.36
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index	249%	
Dermal Intake, mg/kg/day	0.0032	0.288
AIC, mg/kg/day	n/a	n/a
Hazard Index	--	

-----  
 (a) Reference Dose Value (RfD) [1] [5]

(b) no AIC value available

Table C-6

PROPOSED EXPOSURE POINT CONCENTRATIONS (EPCs) AND  
APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS (ARARs)

Pathways	Cyanides	PGDN
Air/Volatilization/Inhalation		
EPC, mg/m3	0.0003 (a) not applicable	
ARAR, mg/m3	0.07 (b)	n/a (c)
Water/Leaching/Ingestion		
EPC, mg/L	0.1 (a) not applicable	
ARAR, mg/L	<del>.700</del> <del>0.2</del> (d)	n/a
Soil/Ingestion		
EPC, mg/kg	4 (a) not applicable	
ARAR, mg/kg	20 (b)	n/a
Soil/Animal Contact/Ingestion		
EPC, mg/kg	0.004 (a) not applicable	
ARAR, mg/kg	n/a	n/a
Soil/Dermal Contact		
EPC, mg/kg	4 (a) not applicable	
ARAR, mg/kg	<del>20</del> (b)	n/a
	n/a	

- 
- (a) EPC values for Cyanides from Table C-2, reduced by 92%
  - (b) Preliminary target concentration for clean closure [7]
  - (c) no ARAR value currently available [1]
  - (d) Drinking Water Standard [1]

TABLE C-7

## CALCULATION OF HUMAN INTAKES FOR PROPOSED REMEDIAL ACTION

Inhalation		
20 cu m/day	70 kg adult	0.29 cu m/kg/day-adult
10 cu m/day	17 kg child	0.59 cu m/kg/day-child
Exposure Point Conc.		
0.00018 mg/cu Cyanides	0.0057 mg/cu m	PGDN
Intake		
0.00005 mg/kg/day-adult	0.002 mg/kg/day-adult	
0.00010 mg/kg/day-child	0.003 mg/kg/day-child	
Ingestion from surface water		
10.0 L/day	70 kg adult	0.000 L/kg/day-adult
0.5 L/day	17 kg child	0.029 L/kg/day-child
Exposure Point Conc.		
0.096 mg/L Cyanides	0.0000 mg/L	PGDN
Intake		
0.0000 mg/kg/day-adult	0.0000 mg/kg/day-adult	
0.0028 mg/kg/day-child	0.0000 mg/kg/day-child	
Ingestion from soil and sediments		
0.000 kg/day	70 kg adult	0.0E+00 kg/kg/day-adult
0.001 kg/day	17 kg child	5.9E-05 kg/kg/day-child
Exposure Point Conc.		
19 mg/kg Cyanides	392 mg/kg	PGDN
Intake		
0.0000 mg/kg/day-adult	0.000 mg/kg/day-adult	
0.0011 mg/kg/day-child	0.023 mg/kg/day-child	
Ingestion of Contaminated Game Fowl or Fish		
0.50 kg/day	70 kg adult	0.007 kg/kg/day-adult
0.25 kg/day	17 kg child	0.015 kg/kg/day-child
Exposure Point Conc.		
0.0043 mg/kg Cyanides	0.4 mg/kg	PGDN
Intake		
0.00003 mg/kg/day-adult	0.003 mg/kg/day-adult	
0.00006 mg/kg/day-child	0.006 mg/kg/day-child	
Dermal Contact with Contaminated Soil and/or Sediments		
0.0 kg/day	70 kg adult	0.000 kg/kg/day-adult
1.0 kg/day	17 kg child	0.059 kg/kg/day-child
Exposure Point Conc.		
0.0043 mg/kg Cyanides	0.4 mg/kg	PGDN
Intake		
0.00000 mg/kg/day-adult	0.000 mg/kg/day-adult	
0.00025 mg/kg/day-child	0.023 mg/kg/day-child	



Table C-8

## RISK CHARACTERIZATION FOR PROPOSED REMEDIAL ACTION

	Cyanides	PGDN
<b>Adults</b>		
Inhalation Intake, mg/kg/day	<del>0.00005</del> <sup>0.00009</sup>	not applicable
AIC, mg/kg/day	0.02 (a)	n/a (b)
Hazard Index	<del>0.24%</del> <sup>0.45%</sup>	
Ingestion Intake, mg/kg/day		not applicable
Surface water	<del>0.00000</del> <sup>28</sup>	
Soil & sediments	0.00000	
Contaminated fish/fowl	0.00003	
Total	<del>0.00003</del> <sup>28</sup>	
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index	<del>0.16%</del> <sup>14.15%</sup>	
Dermal Intake, mg/kg/day	0.00000	not applicable
AIC, mg/kg/day	n/a	n/a
Hazard Index	--	
<b>Children</b>		
Inhalation Intake, mg/kg/day	<del>0.0001</del> <sup>2</sup>	not applicable
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index	<del>0.5%</del> <sup>1%</sup>	
Ingestion Intake, mg/kg/day		not applicable
Surface water	<del>0.0028</del> <sup>23</sup>	
Soil & sediments	<del>0.0011</del> <sup>23</sup>	
Contaminated fish/fowl	0.0001	
Total	<del>0.0040</del> <sup>23</sup>	
AIC, mg/kg/day	0.02 (a)	n/a
Hazard Index	<del>20%</del> <sup>16%</sup>	
Dermal Intake, mg/kg/day	.0.0003	not applicable
AIC, mg/kg/day	n/a	n/a
Hazard Index	--	

(a) Reference Dose Value (RfD) [1]

(b) no AIC value available

## APPENDIX C

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NOTE: Reprints are provided of References [4] and [5], in Appendices D and E, respectively.

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APPENDIX D

"CYANIDES IN THE ENVIRONMENT WITH PARTICULAR  
ATTENTION TO THE SOIL"  
(REPRINT)

## CONFERENCE ON CYANIDE AND THE ENVIRONMENT

Tucson, Arizona - December 1984

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CYANIDES IN THE ENVIRONMENT WITH PARTICULAR  
ATTENTION TO THE SOILby  
Wallace H. Fuller<sup>1</sup>

## ABSTRACT

The frequency in the identification of groundwater and other environment contamination has placed an additional burden on the already overburdened land in the volume of waste that must be accepted for ultimate disposal. If the soils are not effective in confining the wastes, migration of hazardous constituents into groundwater and food chains will occur. As a result of this vulnerability, the soil as a waste treatment/utilization system must receive special research attention. Cyanide-yielding wastes contain some of the hazardous chemicals demanding immediate attention for this soil treatment/utilization effort.

The purpose of this presentation is to provide information regarding the behavior of cyanide and cyanide-yielding chemicals in soils and the surrounding environment under anaerobic and aerobic conditions. In aerobic soils, the most prominent reactions of environmental concern involve nitrification and, in general, the fate of ammonia, nitrite, nitrate, and nitrogen gas. Under anaerobic soil conditions, the most prominent reactions of environmental concern involve attenuation, precipitation as complexes, denitrification, and transport. This presentation centers on these concerns with respect to utilization of cyanide nitrogen by plants at different loading rates, and considers the factors affect nitrification of cyanamid, dicyanodiamid, guanidine and guanidine nitrate, dicyanodiamidine sulfate (guanylurea sulfate), thiourea, and melamine under different soil conditions. In addition, the mobility of KCN (simple form),  $K_3Fe(CN)_6$  (complex form) in aqueous solution, and KCN in natural municipal solid-waste landfill leachate (mixed forms) through five soils of varying physical and chemical properties at rates of 100 and 200 ppm  $CN^-$  is described. The soil characteristics that govern the movement of the various cyanide forms in soils are also described and evaluated.

## INTRODUCTION

New sensitivity toward nature requires us to search for new answers about the environment that surrounds us. A busy area of research, presently, involves the study of toxic wastes in soils. The soil, like the air, is a most abundant natural environmental system

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with which human beings make contact not only directly but indirectly by dust that is breathed, water that infiltrates soil and is pumped for drinking, through food nourished by the soil, as are plants, and animals nourished in turn by plants. The soil has proven to be an acceptable waste receptacle. Cyanamide as a waste is not an exception. Soils will always play an important part in waste disposal despite trends toward recycling of waste constituents. Moreover, the air, rivers and streams must be recognized as overloaded vehicles of waste transport back to the land. Recent sensitivity to and restrictions on disposal methods used heretofore, such as ocean dumping, serve to emphasize the burden that the land must assume. The threat of contamination in underground water resources and food chains can worsen as disposal volume paces populations and industrial expansion. Control measures must be expanded to lessen the threat of environmental pollution. The soil is a key factor in this control.

The soil is the oldest and most effective chromatographic column in the history of the world. Soil is the unconsolidated outer cover of the earth and represents the weathered product of environmental factors at any specific location. Soils differ in characteristics just as do plants and animals. Thus there are prairie and forest soils; thin soils on steep slopes and thick soils on broad ridges; alluvial, residual, and pre-soils. Soils differentiate into horizons, A, B, C, with depth. Each horizon is quite different from the other. Soils also differ greatly from one place to another, yet they perform the same unique activities of biodegrading, precipitating, attenuating, sorbing/desorbing, structuring, and integrating every chemical behavior known, or still unknown, to mankind.

To realize the effectiveness of soil in a waste disposal system as a barrier (though a leaky one) to migration, one should begin with an understanding of the soil properties and the way they interact with wastes and their leachates, and specific pollutants such as toxic constituents. There are three major components of the waste disposal environment which interact in any waste that reaches the earth's surface. These must be identified, described, and quantitatively evaluated. They are:

1. The porous medium through which the constituents are transported (e.g. soil, clay, sand, gravel),
2. The vehicle of transport that carries the polluting constituents or is itself the pollutant (e.g. aqueous leachates, organic solvents, oil etc.), and
3. The specific polluting constituent itself (e.g. soluble heavy metal salts, radionuclides, organic compounds, carcinogens, etc.).

All three are important in management of wastes since they are involved in attenuation of the polluting constituents, interact with each other, and change with time.

#### CYANIDE VERSATILITY

Cyanides appear in a great variety of forms and in a great number of classes of organic and inorganic compounds in nature. Each of the classes contain a cyano group ( $C \equiv N$ ) as part of its molecule.

Taras (1971) refers to cyanide in industrial waste as all of the  $\text{CN}^-$  groups present in the cyanide compound that can be determined as cyanide ion,  $\text{CN}^-$ , by the Liebig distillation method. The  $\text{CN}^-$  ion is a negatively charged, diatomic species with a sigma bond, two pi bonds, and two empty pi anti-bonding orbitals. These bondings give cyanides unusual properties, particularly in metal-cyanide complexes (Huiatt, et al., 1983).

Cyanides may be classified into four broad groups for this discussion:

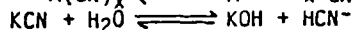
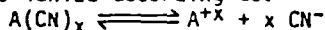
1. Free cyanides -  $\text{CN}^-$  and  $\text{HCN}$

In solution the relationship is highly pH dependent

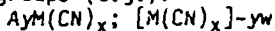


(Figure 1). The  $\text{pK}_a$  of  $\text{HCN}$  is at pH 9.367 where the concentrations of  $\text{CN}^-$  and  $\text{HCN}$  are equal.

2. Simple cyanides -  $\text{A}(\text{CN})_x$  where A is an alkali or a metal and x is the valence of A and represents the number of cyano groups present. Cyanide ions are released when alkali cyanides ionize according to:



3. Complex cyanides -  $\text{AyM}(\text{CN})_x$  where: A is the alkali, y is the number of alkalis ( $\text{Na}$ ,  $\text{K}$ ,  $\text{NH}_4$ ); M is the heavy metal ( $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Ag}^{++}$ , etc.) and x is the number of CN groups equal to the valence of A taken y times plus the valence of the heavy metal. Soluble complex cyanides dissociate into complex ions and not CN groups (e.g.):



w is the oxidation state of A in the original molecule. Further dissociation can take place releasing  $\text{CN}^-$  ions. Again this reaction is highly pH dependent (Figure 1).

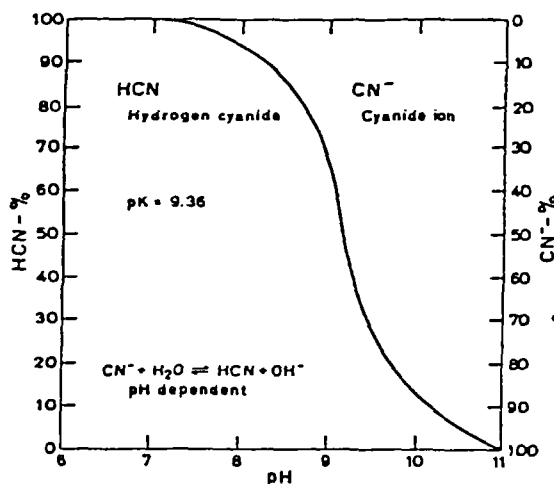


Figure 1. The effect of pH on dissociation of hydrogen cyanide.

4. Organic cyanide-yielders - Represented by cyanogenic (nitriles) glycosides. Glycosides yield one (or more) sugar and one (or more) other compound (e.g. aglycones) when hydrolyzed in vitro by dilute mineral acids or in vivo by enzymes. They are widely distributed in nature.

Cyanides vary in stability in water as illustrated in Table 1 (Scott, 1981). Because of the toxicity of  $CN^-$ , the formation of a more stable cyanide has been a significant factor in the activity of biological systems. At the normal pH's and temperatures of streams, the dissociated cyanide ion ( $CN^-$ ) is toxic to most species of fish at a level of 0.1 mg/liter. Complexed cyanides are far less toxic, and discharge of relatively large concentrations of these compounds to receiving streams is not immediately harmful. Consequently, it has been suggested that cyanide be complexed with metals such as iron, prior to discharge, to reduce toxicity.

#### CYANIDE DISTRIBUTION IN NATURAL ENVIRONMENTS

##### PLANTS

Cyanide-yielding organic compounds are introduced naturally into the environment, particularly the soil, by a great number of living systems. One of the most common natural sources originates from plants (Table 2). Over 800 species of plants (70 to 80 families) synthesize cyanogenic glycosides (Knowles, 1976). They are characterized most abundantly by the glycosides that yield hydrocyanic acid (HCN) upon hydrolysis. One of the best known cyanogenetic (or cyanophoric) glycosides occurs in members of the Rosaceae family and are called amygdalin (Kingsbury, 1964). The chemical reaction is diagrammed in Figure 2. The amount of amygdalin glycoside accumulated by a single plant varies between species, depending on environmental conditions--for example, plants that have wilted, frosted, or have been stunted are most suspect in the incidence of HCN rumen poisoning than unstressed plants.

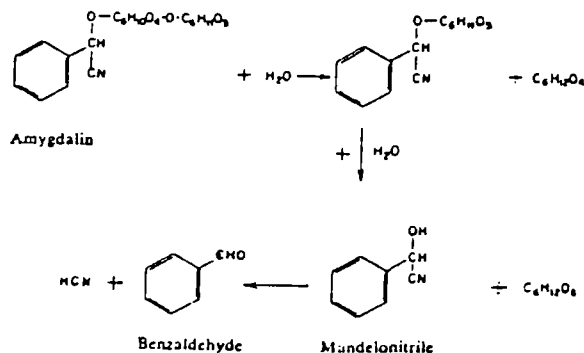


Figure 2. Pathways in the hydrolysis of a cyanogenic glycoside, Amygdalin, yielding HCN

Higher plants have the capacity to metabolize sublethal doses of

administered cyanide (Towill, et al., 1978), as have animals. There is belief that all higher plants possess this ability through a reaction between various forms of sulfur (polysulfides and thiosulfate) such as:

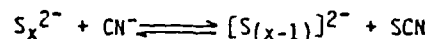


TABLE 1. Relative stabilities of some common cyanide complexes in water

Stability ratings in water	Examples of cyanides in processing solutions
1. Free cyanide	CN <sup>-</sup> , HCN
2. Simple compounds	
a. readily soluble	NaCN, KCN, Ca(CN) <sub>2</sub> , Hg(CN) <sub>2</sub>
b. relatively insoluble	Zn(CN) <sub>2</sub> , CuCN, Ni(CN) <sub>2</sub> , AgCN
3. Weak complexes	Zn(CN) <sub>4</sub> <sup>2-</sup> , Cd(CN) <sub>3</sub> <sup>-</sup> , Cd(CN) <sub>4</sub> <sup>2-</sup>
4. Moderately strong complexes	Cu(CN) <sub>2</sub> <sup>-</sup> , Cu(CN) <sub>3</sub> <sup>2-</sup> , Ni(CN) <sub>4</sub> <sup>2-</sup> , Ag(CN) <sub>2</sub> <sup>-</sup>
5. Strong complexes	Fe(CN) <sub>6</sub> <sup>4-</sup> , Co(CN) <sub>6</sub> <sup>4-</sup> , Au(CN) <sub>2</sub> <sup>-</sup>

TABLE 2. Selected Plants with Cyanogenic Potential

Species name	Common name
<u>Acacia greggii</u>	catclaw
<u>Bahia oppositifolia</u>	bahia
<u>Cercocarpus spp.</u>	mountain mahogany
<u>Florestina tripteris</u>	florestina
<u>Glyceria striata</u>	fowl mannagrass
<u>Holcus lanatus</u>	velvet grass
<u>Hydrangea spp.</u>	hydrangea
<u>Linum spp.</u>	flax
<u>Lotus corniculatus</u>	birdsfoot trefoil
<u>Manihot esculenta</u>	cassava
<u>Phaseolus lunatus</u>	lima bean
<u>Prunus spp.</u>	cherries
<u>Pyrus malus</u>	apple
<u>Sorghum spp.</u>	sudan grass, Johnsongrass, etc.
<u>Stillingia trecaleana</u>	queen's delight
<u>Suckleya suckleyana</u>	poison suckleya
<u>Trifolium repens</u>	white clover
<u>Triglochin spp.</u>	arrowgrass
<u>Vicia sativa</u>	vetch seed
<u>Zea mays</u>	maize, corn

#### MICROORGANISMS



It has been postulated that cyanides accumulate in soils via biological degradation of plants that produce abundant cyanogenic glycosides, such as sorghum (Raugaswami, et al., 1962). Cyanides may also be generated by a great number of soil microorganisms including fungi, bacteria, actinomycetes, and algae. Each (1956), for example, identified 31 fungal species and many genera that elaborate cyanogenic glycosides. Many well known bacteria possess this capacity (Michael and Corpe, 1965; Knowles, 1976).

When the hypothesis for cyanide accumulation was tested by Strobel (1967) using  $^{14}\text{C}^{15}\text{N}$ , he found that the soils most active in utilizing cyanides were those associated with plants that produced cyanogenic glycosides most abundantly. Moreover, nonsterile soil converted cyanide to carbonate and nitrate, whereas sterile soil did not appreciably alter cyanide. Many bacteria, fungi, and algae are capable of utilizing cyanides (Strobel, 1967; Allen and Strobel, 1966; Ware and Painter, 1955; and Towill, et al., 1978, to name a few). Not only is there chemical evidence for cyanide transformation and degradation but there is enzymatic evidence. Cyanides do not accumulate in soils under natural conditions.

#### SOILS

Cyanides are introduced into the soil from natural sources and through the activities of mankind. The cyanides from natural sources do not persist in the soil. The relatively small amounts produced are readily attacked by soil microorganisms and converted to carbonate and ammonia. The soil microorganisms rarely, if ever, leave organic compounds immune to biodegradation. Some cyanide may be released to the atmosphere and dispersed depending on the pH and red/ox of the soil environment. For example, an anaerobic autotrophic actinomycetes species common to sewage, was identified (Ware and Painter, 1955) which grows well on silica gel containing only KCN as a carbon and nitrogen source. The high chemical reactivity of most cyanide also does not permit the accumulation of any significance. Cyanide ( $\text{CN}^-$ ), up to 200 ppm at least, is readily converted to fertilizer nitrogen in the soil (Fuller, et al., 1950a). In fact, levels of many cyanides equivalent to the nitrogen requirements of cultivated crops support plant response, which is almost identical to that from other nitrogen sources such as sodium or ammonium nitrate on an equivalent N basis (Fuller, et al., 1950b).

Cyanide is one of nature's most toxic substances. The level of toxicity of the more stable cyanides depends on the metal present and on the proportion of  $\text{CN}^-$  groups converted to simpler alkali cyanides. The estimated concentration of cyanide ( $\text{CN}^-$ ) in waste streams of cyanide users, varies from 100 to 50,000 mg/l depending on the efficiency of the manufacturer and process used (Rudolph, 1953). Although the numerous cyanides discharged as wastes differ from each other with respect to their impact on the environment, the loading rate in soil is the paramount factor determining toxicity to microorganisms or hazard for movement into groundwater and food chains. High concentrations in the environment usually are associated with accidental spills or improper waste disposal (Towill et al., 1978).

According to The Chester Engineers (1979) cyanide volatilizes at a rate of 0.021 mg CN/ft<sup>2</sup>-hr from still water surfaces containing a concentration range of 0.1 to 0.5 mg/L.

#### CYANIDE REACTIONS IN THE SOIL

##### NATURAL SOURCES

The soil as a weathered system does not contain cyanides nor does it generate cyanides, except indirectly in supporting the growth of microorganisms, plants, and other intimate soil life. In fact, soil organic matter inactivates the toxic effects of cyanide as a result of its affinity for combining. Cyanides that enter the soil from the low-level natural sources are rapidly biodegraded and quickly metabolized by soil microorganisms. Strobel (1967) was unable to isolate cyanides from soils growing sorghum, a plant that not only produces cyanogenic glycosides in abundance but grows luxuriously to yield large amounts of plant residue.

##### PESTICIDES

Pesticides are examples of many cyanides and cyanide-yielding substances that end up in the soil environment over large areas for beneficial use. A list of pesticides, grouped according to six general classes that either contain cyanide radicals or may be metabolized into yielding cyanide radicals, has been compiled in Table 3. Four general groups were identified: dithiocarbamate, triazine, triazol, and pyrethroid. In addition, cyanide capsules and calcium cyanide are used for special purposes. Despite their regular use on agricultural crops and noncrops, cyanides do not accumulate. They biodegrade easily and convert readily to harmless constituents, and some of them even end up becoming valuable nitrogen (HN<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) plant nutrients. The soil microorganisms quickly take advantage of the low levels of readily metabolizable energy sources that reach the soil as a result of pest control applications. Because of this, the compounds listed in Table 3, which represent at least 24 individual marketed pesticides, are considered as among the safest commercial agricultural chemicals used to improve food and fiber production.

##### FERTILIZERS

###### Establishment of Cyanides as Fertilizers

The realization that cyanides can be used as fertilizers for agricultural crops is not new. Pioneers of this practical application date back to Miller, 1906; Robine, Lenglen, and LeClere, 1906; Cowie, 1919a,b). And again in 1945a,b). At about this same time, an extensive laboratory and field study was undertaken in Arizona to compare the nitrifying characteristics of some cyanides and cyanide-yielding compounds (Table 4) for commercial fertilizer purposes (Fuller et al., 1950a,b). Calcium cyanamide, dicyanodiamide, guanidine nitrate, guanylurea sulfate, and thiocurea were found to nitrify rapidly and compare favorably with the more conventional fertilizers, ammonium sulfate and urea, in Arizona soils when applied at a rate of 100 and

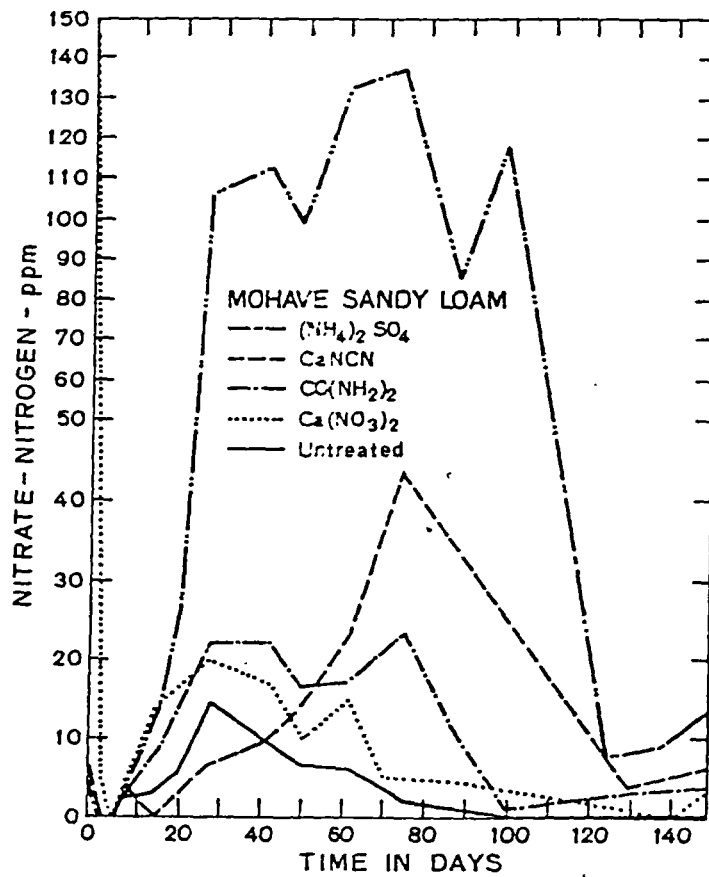
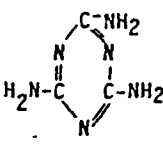
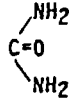


Figure 3. Change with time of nitrate-nitrogen in Mohave sandy loam treated with various nitrogen fertilizers.

TABLE 3. A list of pesticide categories that either contain cyanide radicals or may be metabolized into yielding cyanide radicals.

Chemical Class	Name	Use	Application
1	Dithiocarbamate	fungicide	fruits, melons, grains, vegetables, fiber crops
2	Triazine	herbicide	non-crops, grains, alfalfa, fiber crops
3	Triazine	fungicide	melon, vegetables
4	Triazole	herbicides	non-crops, grains, ornamentals
5	Triazole	fungicides	apples, barley, grapes, wheat
6	Pyrethroid	insecticides	experimental use, cotton, apples, corn, pecans

TABLE 4. Selected nitrogen and/or cyanide yielding compounds that have soil fertilizer value.

Name	Formula
• Ammonium Sulfate	$(\text{NH}_4)_2\text{SO}_4$
• Cyanamide	$\text{H}_2\text{N}-\text{C}\equiv\text{N}$
• Dicyanodiamide	$\text{NH}_2-\text{C}(\text{NH})_2-\text{CN}$
• Guanidine Nitrate	$\text{CH}_5\text{N}_3 \cdot \text{HNO}_3$ $\text{HN}=\text{C}(\text{NH})_2 \cdot \text{HNO}_3$
• Guanyurea Sulfate or Dicyanodiamidine Sulfate	$(\text{NH}_2-\text{C}(\text{NH})_2-\text{C}(\text{NH})_2-\text{NH}_2) \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
• Thiourea or Thiocarbamide	$\text{H}_2\text{N}-\text{C}(\text{NH}_2)=\text{S}$
• Melamine or Cyanurotriamide	
• Uramon or Urea	

200 ppm N (Tables 5 and 6). Melamine biodegrades so slowly it has questionable value as a fertilizer (Table 5). Calcium cyanamide, added to soil in amounts of 50- to 100 lbs N/A-6 inches under field conditions of wheat and barley production, was also found to be approximately equivalent to conventional commercial fertilizers, Figure 3, (Fuller, et al., 1950a,b). The nitrification rate of calcium cyanamid, for example, compared favorably with urea (Fuller, et al., 1950b; Fuller, 1963; and Volk, 1950). Application of 140 and 250 lbs N/A in the form of calcium cyanamid to Yuma Superstition sand and Mesa Laveen clay loam, supported highly significant barley grain yields over the no-fertilizer control soil (Table 7).

#### Nitrification Rates of Cyanide-Yielding Compounds

Some inhibition in the rate of conversion from ammonia to nitrate occurred with cyanamide, dicyanodiamide, and thiourea at an application of 200 ppm N but not at the 100-ppm N rate under laboratory conditions. The data clearly revealed that certain cyanogenic compounds were inhibitory to the *nitrosomonas* and *nitrobacter* that convert ammonia to nitrate but did not inhibit the microorganisms that transformed the compounds to ammonium (Tables 5 and 6). Since the  $\text{NO}_3^-$  ion is much more mobile than  $\text{NH}_4^+$ , the principle of slowing down the nitrification of  $\text{NH}_3$  led to the commercial development of compounds that would inhibit nitrate formation from ammonia to delay or reduce fertilizer loss by migration through soils beyond the reach of plant roots. This favorable fertilization principle is demonstrated in the residual effect of nitrogen to the second-season crop from thiourea and cyanamid when applied to barley in field experiments, Table 7 (Fuller et al., 1950a), but this effect did not occur when the fertilizers were ammonium sulfate or urea.

#### Simple Cyanides as Fertilizers

Sodium cyanide was reported to be only slightly less effective than sodium nitrate as a nitrogen fertilizer for corn, tobacco, and mustard when used on nitrogen-deficient soils (McCool, 1945a,b). Potassium cyanide also has soil fertilizing qualities since it nitrifies rapidly in soils to yield  $\text{CO}_2$  and  $\text{NH}_3$  (Strobel, 1967). Cyanides may be fixed by soil organisms in several ways. All give rise to some organic nitriles, which in turn yield ammonia with the corresponding organic acids (Strobel, 1967).

#### Anaerobic Cyanide Reactions

Microbial reactions under anaerobic soil conditions (e.g. water-logging) are quite different from those under aerobic conditions. Soil microorganisms responsible for degrading cyanide under anaerobic conditions are believed to be more sensitive to the concentrations tolerated under aerobic conditions. The limit of tolerance for effective anaerobic degradation was suggested by Coburn (1949) as 2 ppm. Thus, the opportunity for cyanides to move through soil is expected to be greater under anaerobic than aerobic environmental conditions. Since denitrification of cyanides under anaerobic soil environments is not well known, it is not wise to speculate too freely

Table 5. Changes with time in pH value, ammonium-, nitrite-, and nitrate-nitrogen content of Mohave fine sandy loam receiving various cyanide-yielding organics applied at 200 ppm.

30

Incubation Period days	Ammonium Sulphate 200 p.p.m. of N				Uramon 200 p.p.m. of N				Cyanamid 200 p.p.m. of N				Dicyanodiamid 200 p.p.m. of N				Guandine Nitrate 200 p.p.m. of N				
	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	
0	7.8	200	1	0	8.0	20	Trace	1	8.1	18	Trace	1	7.8	8	0	1	7.8	8	Trace	1	89
8	7.3	186	0	13	7.7	183	0	7	8.4	97	0	0	7.8	18	0	0	7.8	18	0	0	89
9	7.2	90	78	77	7.3	101	82	86	8.1	128	Trace	37	7.9	13	0	18	7.8	11	Trace	0	83
17	7.3	44	84	93	7.3	89	107	87	8.1	128	Trace	37	7.9	13	0	18	7.8	11	Trace	0	83
22	7.3	0	0	148	7.0	10	10	100	8.1	140	Trace	18	7.9	17	0	18	7.8	10	Trace	0	81
25	7.4	13	Trace	178	7.4	0	Trace	192	8.2	133	Trace	21	8.0	17	0	23	7.8	10	Trace	0	95
28	7.8	0	Trace	223	7.7	0	Trace	208	8.0	143	Trace	22	7.9	18	0	24	7.8	7	Trace	0	183
36	---	---	---	---	---	---	---	---	8.1	137	Trace	23	---	---	---	---	---	---	---	---	---
43	---	---	---	---	---	---	---	---	8.1	128	Trace	24	---	---	---	---	---	---	---	---	---
87	---	---	---	---	---	---	---	---	8.1	128	Trace	31	---	---	---	---	---	---	---	---	---
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\*Parts per million on basis of soil.

†Nitrate-nitrogen values were negative for reasons not yet understood.

Incubation Period days	Guanylsulphate 200 p.p.m. of N				Thiourea 200 p.p.m. of N				Melamine 200 p.p.m. of N				Untreated			
	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm	pH	NH <sub>4</sub> -N ppm*	NO <sub>2</sub> -N ppm	NO <sub>3</sub> -N ppm
0	7.7	9	Trace	3	7.8	10	0	1	7.8	8	Trace	1	7.8	8	Trace	3
8	7.8	10	0	0	8.0	31	0	1	7.7	8	Trace	0	7.8	8	Trace	0
9	7.8	12	Trace	30	8.0	25	0	0	7.8	8	Trace	0	7.8	8	Trace	18
17	7.8	14	0	23	8.1	39	0	0	7.9	8	Trace	0	7.8	8	Trace	31
22	7.3	13	0	31	8.0	90	0	0	8.0	9	Trace	0	7.9	8	Trace	37
29	7.3	13	0	31	7.8	115	0	0	7.8	8	Trace	0	7.8	8	Trace	41
42	7.3	13	0	31	7.8	68	0	0	7.8	8	Trace	0	7.8	8	Trace	41
57	---	---	---	---	7.7	115	0	0	---	---	---	---	---	---	---	---
87	---	---	---	---	7.7	135	0	0	---	---	---	---	---	---	---	---
87	7.8	7	0	39	7.8	138	0	0	7.8	3	Trace	0	7.8	13	0	33
90	7.4	3	0	128	7.8	160	0	0	7.8	3	Trace	0	7.8	13	0	44
97	7.4	3	0	178	---	---	---	---	---	---	---	---	---	---	---	---
111	7.4	8	0	283	---	---	---	---	---	---	---	---	---	---	---	---
120	7.8	8	0	240	---	---	---	---	7.8	0	Trace	0	7.8	4	0	84
159	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
202	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
248	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
370	---	---	---	---	---	---	---	---	7.7	0	Trace	0	7.7	2	Trace	70

\*Parts per million on basis of soil.

†Nitrate-nitrogen values were negative for reasons not yet understood.

TABLE 6. Changes with time in pH value, ammonium-, nitrite-, and nitrate-content of Mohave fine sandy loam receiving cyanamide and thiourea applied at 100 ppm.

Incubation Period days	Cyanamide 100 p.p.m.* of N				Thiourea 100 p.p.m. of N			
	pH	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N	pH	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N
		ppm*	ppm	ppm		ppm*	ppm	ppm
0	8.7	28	Trace	15	8.0	11	Trace	1
4	8.1	79	Trace	15	8.0	3	0	1
11	8.2	79	2	17	8.0	29	0	1
14	8.0	72	Trace	23	8.0	44	0	1
18	8.1	62	1	20	8.0	57	0	4
39	7.9	58	0	37	7.9	87	Trace	18
67	7.6	1	0	104	7.5	45	8	21
70	7.7	10	0	100	7.5	36	Trace	64
79	—	—	—	—	—	—	—	—
90	—	—	—	—	—	—	—	—
122	—	—	—	—	—	—	—	—
152	—	—	—	—	—	—	—	—
198	—	—	—	—	—	—	—	—
322	—	—	—	—	—	—	—	—

\*Parts per million on basis of soil.

†Nitrate-nitrogen values were negative for reasons not yet understood.

TABLE 7. The influence of some cyanogenic fertilizers on barley grain yields from two calcareous soils.

Material Added	Increase in Barley Due to Nitrogen Application	
	Laveen clay loam	Superstition sand
	%	%
None	...	...
Dicyanodiamide	3.1	...
Guanylurea sulfate	7.5	...
Guanidine nitrate	27.8*	0.5
Ureaform N-20	30.6*	8.0
Ammonium sulfate	32.6*	38.8*
Ureaform N-40	40.3*	20.8*
Cyanamide	45.3*	52.4*
Thiourea	62.3*	62.4*

\*Highly significant increase, 1% level.

and interpret significance much beyond what is actually known. But there is evidence that the denitrification process does occur in certain soluble cyanides and that it yields N<sub>2</sub> gas, probably through nitrates under limited free O<sub>2</sub> conditions, and particularly, where sulfur compounds are available (Huiatt, 1983, Ch.2).

#### LANDFILLS

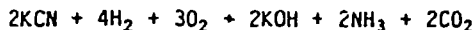
Untreated cyanide disposals to landfills are not allowed under the present regulations. However, cyanide wastes that have been placed in drums during some former period may pollute the soil environment through leakage. Should such occur, remedial procedures must be initiated to confine the chemical (Tolman et al., 1978). The real problem centers around toxicity since concentrations may be expected to be higher than just discussed with soil fertilization. Microbial degradation rates and the attenuation capacity of the soil could be exceeded.

## LAGOONS, PONDS, AND WASTE WATEKS

One of the oldest methods of confining mining and plating cyanides, preventing their movement to the surrounding environment, is the establishment of shallow earth lagoons and ponds. Such facilities designed for deep soils of fine textures, clay-lined and deep watertables, have been quite successful in confining cyanides. Shallow ponds of low-level cyanides exchange gases readily with no appreciable limitation of oxygen sufficient to convert cyanides readily to nitrates. In fact, the accumulation of nitrates may pose a greater problem to underground water quality than cyanides. Fortunately, another mechanism is available in properly designed mining lagoons and ponds that is centered in the clay lining and acts as an anerobic denitrifying barrier to underground flow similar to that in a rice paddy. The nitrates denitrify at this low red/ox juncture in the bottom of the pond with the discharge of harmless  $N_2$  gas into the atmosphere.

The threshold limit of  $CN^-$  toxicity on biological activity of aqueous systems varies widely with such environmental factors as water quality, temperature, type and size of the organism. Thus, definite effects cannot be established except in terms of the nature of the effects. For example, Lockette and Griffiths (1947) report that 5.0 ppm of  $CN^-$  in sewage treated by the activated process had a marked depression effect on the purification process, whereas Ludzack et al. (1951) found inhibition effects as low as 0.3 ppm under certain other conditions. In concentrations of 6%  $CN^-$ , all waters studied were purified up to 50% or more of the control within 10 days of incubation.

Of particular interest because of its toxicity to the cytochrome system is the utilization of cyanide by specific microorganisms found in wastewaters. Ware and Painter (1955) isolated an aerobic autotrophic actinomycete from sewage which is capable of growing on silica containing only KCN as a source of carbon and nitrogen. This organism can utilize concentrations of  $CN^-$  up to 15 mgm/100 ml but grows more favorably at 4 mgm/100 ml concentrations. The rate of utilization in colony culture approached a maximum of 0.5 mgm  $CN^-$ /day. Presumably the general reaction proceeds as follows:



Other examples of specific microbial assimilation and transformation of  $CN^-$  in synthetic media (not soil) are those given by Keynolds (1924), Strobel (1964), and Allen and Strobel (1966).

## CYANIDE MOVEMENT IN THE SOIL

## SCOPE

Since many of the cyanide wastestreams, waste ponds, lagoons, and leachates end in an anoxic soil environment, a fundamental research program was undertaken to study cyanides under anaerobic soil conditions with specific objectives:



. To study the rate of degradation of simple and complex cyanide under saturated and unsaturated (70% of field water-holding capacity) soil conditions.

. To evaluate the influence of different organic energy sources on the rate of degradation or transformation of cyanides.

. To study the mobility of certain cyanides, in water and municipal landfill leachate, through soils with distinctly different chemical and physical properties, in order to statistically relate soil parameters to observed attenuation and degradation.

#### SATURATED ANAEROBIC SOIL CONDITIONS

##### Experimental

Three sets of four different soils (Table 8) were packed in a pvc column 5 cm in diameter and 12 cm long to a specified bulk density (Fuller, 1982; Fuller and Warrick, 1984a,b). Each set was connected to one of three constant head devices and each one contained a different cyanide solution. Solution #1 contained potassium cyanide in water; solution #2 contained potassium cyanide in a landfill leachate, and solution #3 contained a complex form of cyanide in deionized water alone, Table 9 (Alesii, 1976; Alesii and Fuller, 1976).

TABLE 8. Reference Soils Used in the Cyanide Movement Research

Series* Soil	Order Soil	Clay		Free Iron	Soil pH	Cation Exch. Capacity	Elec. Cond.of Extract	Bulk Density
		%	%	%		meg/100g	$\mu\text{mhos/cm}$	$\text{g/cm}^3$
Molokai	Oxisol	52	25	23.0	6.2	14	1262	1.44
Nicholson	Alfisol	49	47	5.6	6.7	37	176	1.56
Mohave(Ca)	Aridisol	40	28	2.5	7.8	12	510	1.54
Ava	Alfisol	31		4.0	4.5	19	157	1.44

\*Oriented on basis of clay content.

The flow of the solution was regulated to provide approximately one pore volume of displacement each day. The displacements were continued until 20 pore-space volumes were collected. The effluent was collected each day in a 125 ml bottle containing 5 ml of 1N sodium hydroxide. The sodium hydroxide was necessary to keep the cyanide that comes through with the solution from volatilizing. The solution collected was analyzed for total cyanide by the Liebig distillation method according to Taras (1971).

The distillation of the sample was required to convert all the complex cyanide in the sample into simple cyanide ions. The sample was then easily analyzed by the Liebig titration method using silver nitrate and Rhodanin indicator (when the concentration was above 1 ppm). When the concentration was below 1 ppm, the Liebig colorimetric method involving pyridine-pyrazalene was used.

TABLE 9. Characteristics of Cyanide Solution Used in the Movement Research

Cyanide solution	pH of solution	Concentration of cyanide in solution mg/L	Type of ion present
KCN in deionized water	10.0	97	CN <sup>0</sup>
K <sub>3</sub> Fe(CN) <sub>6</sub> in deionized water	8.5	98	Fe(CN) <sub>6</sub> <sup>0</sup>
KCN in landfill leachate	5.4	80	Unknown (mixed)

#### Discussion

The relative mobility of the three cyanide solutions is best illustrated in Mohave (Ca) clay loam and Kalkaska sand (Figure 4). All data are plotted as pore volume versus  $C/C_{max}$ , where  $C/C_{max}$  is the ratio of effluent concentration to influent concentration. KCN and K<sub>3</sub>Fe(CN)<sub>6</sub> in deionized water were both found to be very mobile in soils, while KCN in landfill leachate was the least mobile of the three solutions.

The effect of soil type on the movement of the three cyanide solutions is illustrated in Figure 5, showing the amount of KCN in deionized water that was leached through four soils. The CN<sup>0</sup> was retained most by soils having a high concentration of Mn and hydrous oxides of Fe (Nicholson silty clay and Molokai clay). Korte et al. (1975) found similar results working with the anion forms of As, Cr, Se, and V. This conclusion is further supported by data from Berg and Thomas (1959). They found Cl<sup>0</sup>, which is similar to CN<sup>0</sup> in its adsorption behavior, attenuated in soils having a high percentage of kaolin clay and iron and aluminum oxides. Schofield (1939) also reports that soils high in these oxides have a high anion exchange capacity. Kamprath (1956) found good retention of SO<sub>4</sub><sup>2-</sup> by an acidic soil high in oxides and kaolin, whereas the 3-layer minerals appeared to have relatively poor retention for SO<sub>4</sub><sup>2-</sup>. The acidic soil (Ava silty clay loam) in this study proved, on the contrary, to be a poor attenuator of CN<sup>0</sup>. Texture seems to have little measurable effect on the attenuation of KCN. Free iron oxide and CaCO<sub>3</sub> seem to have a greater influence on the movement of KCN in water than either soil pH or texture.

Figure 5 illustrates the movement of K<sub>3</sub>Fe(CN)<sub>6</sub> in deionized water through four soils (Mohave (Ca) clay loam, Ava silty clay loam, Nicholson silty clay loam, and Kalkaska sandy loam). The ferricyanide ion also migrated most rapidly through soils having a high pH and in the presence of free CaCO<sub>3</sub> (Mohave (Ca) clay loam) for the same reason as KCN in water. Ferricyanide moved slowest in soils having a low pH (Ava silty clay loam and Kalkaska sandy loam). A low pH would indicate the clay surface to have a high percentage of positive exchange sites which would attract the Fe(CN)<sub>6</sub><sup>3-</sup> ion and retain it. Texture seems to play a more important role in this case.

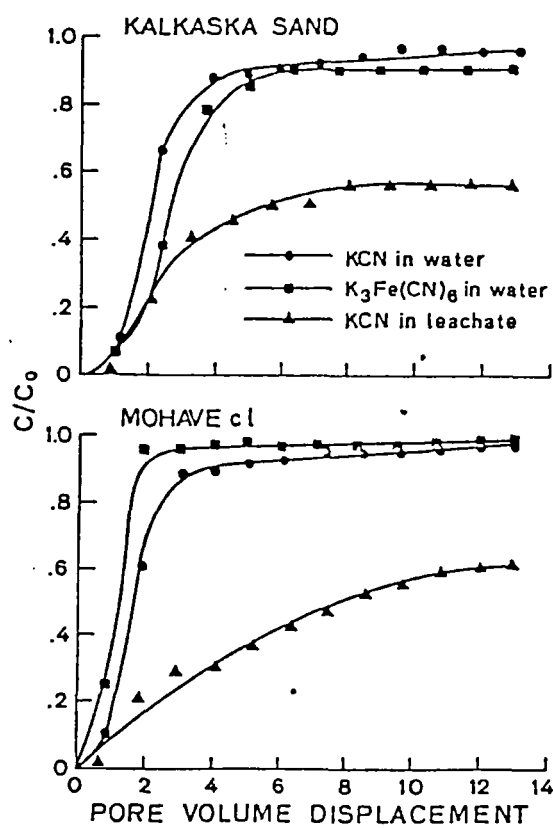


Figure 4. Relative mobility of three cyanide solutions (water and leachate) through Kalkaska sandy loam and Mohave (Ca) clay loam.

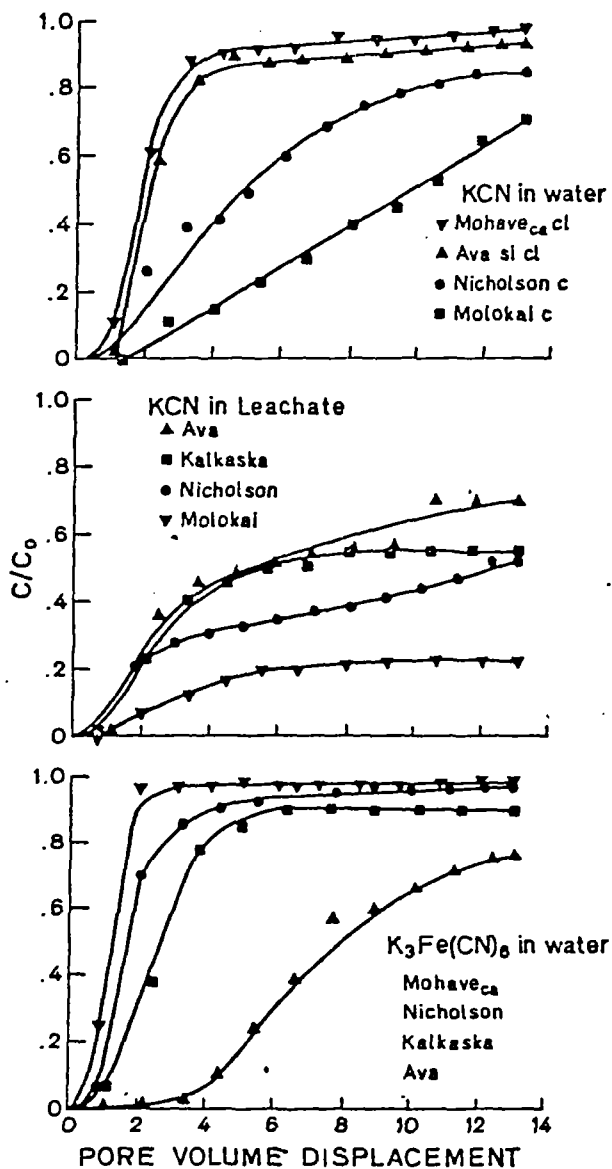


Figure 5. Effects of soil type on the mobility of KCN in water and leachate and  $K_3Fe(CN)_6$  in water

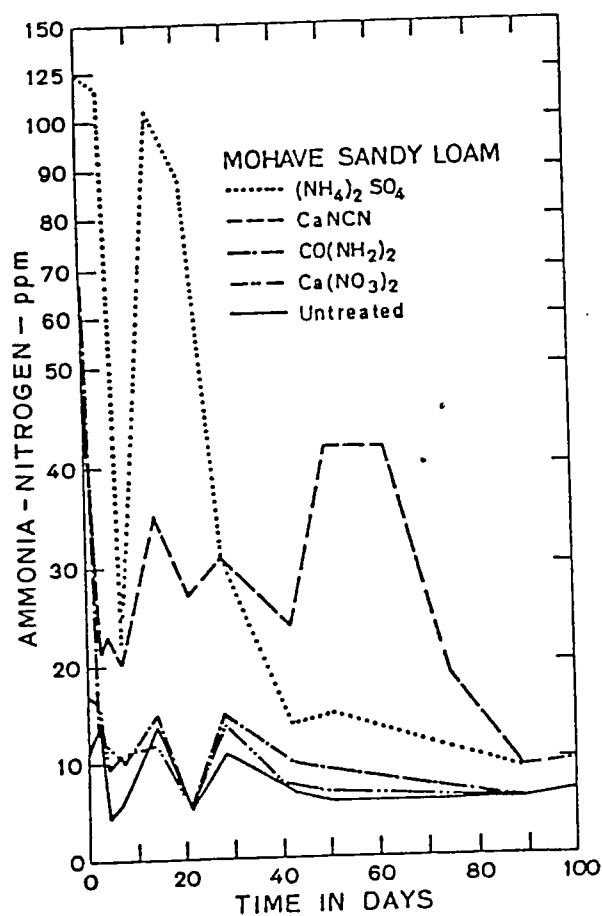


Figure 6. Change with time of ammonia-nitrogen in Mohave sandy loam treated with various nitrogen fertilizers

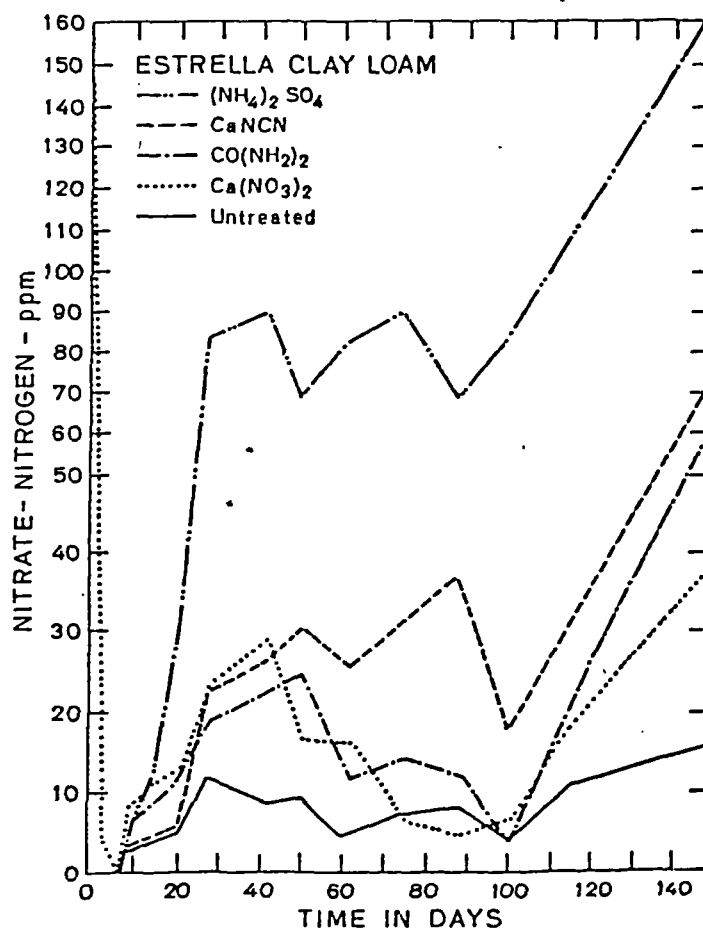


Figure 7. Changes with time of nitrate-nitrogen in Estrella clay loam treated with various nitrogen fertilizers

The high clay content soil (Ava silty clay loam) retained more of the  $\text{Fe}(\text{CN})_6^{3-}$  than the sandier soil of similar pH (Kalkaska sandy loam). Although iron-oxide seemed to have some affinity for  $\text{Fe}(\text{CN})_6^{3-}$ , its presence was not as effective as soil pH in governing the movement of this form of cyanide.

KCN in MSW landfill leachates migrating through the four soils moved through those with the lowest pH (Ava silty clay loam and Kalkaska sandy loam). Cyanide was retained most extensively by soils having a high concentration of iron-oxide (Figure 5).

Of the three cyanide solutions, KCN in MSW leachate was found to move through the soils most slowly. This can be explained partly by the precipitation of Prussian blue when KCN was added to the leachate (Robine et al., 1906). This blue precipitate was found infiltrating the top 4 cm of the soil columns. The accumulation indicates that Prussian blue may be quite immobile in soils. The cyanide that came through the soil was the  $\text{CN}^-$  that did not react with the Fe in solution to form Prussian blue.

The anaerobic state of the soil columns inhibited microbial degradation of cyanide. Microorganisms responsible for degrading cyanide under anaerobic conditions are very sensitive to an elevated concentration of this compound. The limit for effective anaerobic degradation of cyanide was found by Coburn (1949) to be 2 ppm in the wastestream, a concentration much lower than the approximate 100 ppm that passed through the soil columns. The incubation studies, therefore, were negative with respect to cyanide degradation, i.e. degradation did not occur significantly in the water-saturated, anaerobic soil. Nitrate, nitrite, and ammonium were not found as a result of possible  $\text{CN}^-$  transformation; but there was no measurement of  $\text{N}_2$  gas for the detection of denitrification.

#### UNSATURATED, AEROBIC SOIL CONDITIONS

The cyanides react quite differently under aerobic than anaerobic soil conditions. The differences are apparent by comparing migration or movement in anaerobic soil columns with the same soils under field conditions where cyanide-yielding compounds rapidly ammonify and nitrify. Calcium cyanamide, for example, ammonifies more rapidly than urea and nitrifies comparably to ammonium sulfate and more rapidly than urea in Mohave sandy loam under field conditions (Figures 3 and 6). Nitrification of calcium cyanamide also progresses well in Estrella clay loam (Figure 7). Cyanide was not detected in soil deeper than 20 cm (8 in) or beyond the layer of cyanide incorporation. Soils in Mesa and Yuma, Arizona, also were sampled every 10 days throughout the barley growing season for detection of the original material, cyanide, or cyanide-related compounds (Table 5). None of these were found within or below the incorporation layer, except for the traces from the original substances (cyanamide, dicyandiamide, guanylurea sulfate, guanidine nitrate, thiourea) in the 8-inch incorporation layer only, found immediately after being applied. However, nitrate-nitrogen, attributable to the application of fertilizers and cyanides, was detected to a depth of about 30 cm (12 in) after the first irrigation.

Certain conditions in the field, compared with those in soil columns, also delegate against cyanide movement through the soil; such as,

- Molecular oxygen availability is greater in the field,
- Wetting and drying is more prominent in the field,
- Soil microorganisms are more active under natural conditions,
- Photochemical activity is greater in the field,
- Fluctuation in soil moisture levels is greater in the field.

#### CONCLUDING KEYNOTE STATEMENT

1. Cyanides and cyanide-yielding compounds are found well distributed in the total earth surface environment.
2. Cyanides from widespread natural sources of plants, microorganisms, animals, and infrequently identified in soil, water, and air, originating from biological sources, offer little hazard to the inhabitants of the earth surface environment.
3. Low levels of free cyanides in nature do not persist in soils due to many highly reactive indigenous chemical and enzymatic transformations and degradation processes.
4. Cyanide toxicity originating from natural sources through plant consumption by ruminants has occurred but proper management of feeding and grazing appears to minimize this hazard.
5. Commercial sources of cyanides have proved useful to agricultural crop production as exemplified by pesticides and fertilizers both of which are readily converted to plant nutrient sources such as ammonia and nitrate. Cyanides used for these purposes do not persist in the soil.
6. Free cyanide is one of nature's most toxic substances. Free cyanide, also, is a very reactive ion readily forming insoluble and very slowly soluble complex compounds. The loading rate in soils, therefore, is the paramount factor in determining the hazard for biological systems and movement to ground waters. Simple cyanides have been applied at rates of 280 kgN/ha to aerobic soils as fertilizers with no hazardous effects. In anaerobic soils the "safe" level drops to a few ppm.
7. Adequate knowledge exists for controlling cyanide pollution in soil, water, and air environments.
8. The soil is the first and main line of defense for accidental cyanide spills and inadvertant overloading of disposal areas.
9. The soil factors most responsible for control of cyanides in the environment are: (a) clay content, (b) depth of soil, (c) hydrous oxides of iron, manganese, aluminum and other metals, (d) pH, (e) aerobic conditions, and (f) presence of soil organic matter.



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## DISCUSSION

Comment (W. Fuller): One item I did not bring to your attention, but which is very important, is that as cyanide is used and oxidized, nitrate builds up. Nitrate is a mobile anion, as you know, and the hazard may not be cyanide, but nitrate.

Question (F. DeVries): It seems to me that the levels of cyanide we deal with in disposal problems are an order of magnitude or so less than the hazardous level of nitrates. Is that not correct?

Answer (W. Fuller): I have seen ponds with 500 ppm nitrate in the water, and that is a little high for water to be used as recharge.

Question (F. DeVries): We usually talk about cyanide concentrations in water effluents under a part per million, perhaps less than one tenth of a part per million. My understanding is that nitrate concentrations allowable in potable water approach 10 ppm.

Answer (W. Fuller): That's right, but some of these ponds are continually fed and the nitrate concentration builds up.

Question (P. Saletta): Dr. Fuller, concerning the replacement of soils in the final reclamation of cyanide tailings disposal sites, have there been any studies, that you know of, of possible effects on those replaced soils from the solid waste disposal of cyanide tailings?

Answer (W. Fuller): No, but I'm glad you asked that question. One of the important things about this conference is that, although the soil scientists, the biochemists and the civil engineers are most often located in different buildings and often don't cross-inoculate, here we have finally come to the conclusion that we need to work as a team.

Question: Dr. Fuller, would you say there are any naturally-occurring cyanides in lakes or other water bodies that would build up to toxic levels? If so is that taken into consideration in assessing possible spills?

Answer (W. Fuller): None that I know of.

Comment (R. Walline): I have seen detectable levels of 'natural cyanide', but not toxic levels. So in comparison to a spill, it's usually negligible compared to the industrial component.

Question: Dr. Fuller, theoretically speaking, could it occur?

Answer (W. Fuller): I don't see a great possibility for it. Remember that the high reactivity of cyanides, the biological attack on them and so forth, really limits their accumulation in natural environments. On the other hand, I refer you to Dr. Reed's talk on animals

which may eat plants that have high amounts of glycosides.

Question: If bacteria exist which can decompose cyanide, is it possible that artificial culture of these bacteria might be an eventual solution to the problem of getting rid of cyanide in our tailings ponds?

Answer (W. Fuller): That is a very important item, but there are problems with inoculation. First, the environmental conditions must be specific for that one organism. I gave you an example of an actinomyces that grows in sewage under anaerobic conditions and will grow on potassium cyanide alone. However, if we have the idea of finding that organism and putting it in other sewage, we have to remember that sewages vary considerably. Nevertheless, it's a good point and I'd like to see more research done on it. We have found in biological pure-culture work that it takes a lot of effort and money to support that kind of work, but I would not rule out the possibility. If I find one, I'm going to patent it.

Comment (R. Walline): To follow up on that, later in the week, Terry Mudder from Homestake Mining Company will be speaking. Homestake Mine is using a biological system—a specific bacteria—to treat mining effluent specifically for cyanide, so there is now a system in place doing just what you suggest.

APPENDIX E

"CYANIDE CHEMISTRY" (EXCERPT FROM EPA REPORT)

# **HEAP LEACH TECHNOLOGY AND POTENTIAL EFFECTS IN THE BLACK HILLS**

**EPA CONTRACT NO. 68-03-6289  
WORK ASSIGNMENT NO. 1**

RECEIVED  
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CLEVELAND ES

**PREPARED FOR**

**U.S. ENVIRONMENTAL  
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**SEPTEMBER 30, 1986**

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## CYANIDE CHEMISTRY

### OVERVIEW

Cyanide may occur in many forms. The forms of cyanide relevant to a discussion of heap leach mining are:

Free cyanide - Cyanide ion ( $\text{CN}^-$ ) and molecular hydrogen cyanide (HCN). The distribution between cyanide and HCN is dependent on pH with HCN predominant below pH 9.36 (20° C).

Simple cyanide - an alkali or metal cation and cyanide. An example of a soluble simple cyanide is sodium cyanide (NaCN), which is used in process solutions at heap leach operations.

Complex cyanide - metal cyanide complexes and their salts. Metal cyanide complexes are divided based on their stability into weak complexes containing zinc or cadmium, moderately strong complexes containing copper, nickel, or silver, and strong complexes containing iron, cobalt, or gold. The salts are relatively insoluble.

Cyanogenic glycosides - organic compounds introduced naturally into the soil which release cyanide upon hydrolysis. Plants are one of the most common sources.

Methods for measuring cyanide in water and the species of cyanide detected by each method are:

Free cyanide - measures the amount of HCN and  $\text{CN}^-$ .

Weak acid dissociable cyanide - measures free cyanide, and complexes of Cd, Cu, Ni, Ag, and Zn.

Total cyanide - measures free cyanide, weakly acid dissociable cyanide and most inorganic complex cyanides including Fe but excluding Au, Co, and some of the Pt metals.



Cyanide amenable to chlorination - measures the difference between total cyanide concentration before and after chlorination.

Researchers have been experimenting with different types of leaching and analytical procedures for cyanide measurement in solid samples such as spent ore.

Cyanide is a very reactive and relatively short-lived contaminant. Processes which tend to degrade or transform free cyanide in the environment are volatilization of HCN, reaction of cyanide to form ammonia and formate, oxidation, complexation with metallic ions, biological activity, conversion to thiocyanate ( $\text{SCN}^-$ ) and sorption. Cyanide may be released from simple and complex cyanides depending on the stability of the specific compound or complex. In addition, iron or cobalt cyanide complexes, which are strong complexes, may undergo photochemical degradation by sunlight and release free cyanide. Cyanide released from simple and complex cyanides will be subject to degradation or transformation processes.

Volatilization is probably the most significant process in the natural degradation of cyanide in surface waters. Generally, free cyanide would be more mobile in surface waters with higher pH, lower temperature, lower levels of metals and sulfide, organic and inorganic suspended matter, and which have little interaction with sediment. Surface water bodies with stagnant, deep conditions and little surface area would promote high mobility of cyanide. Volatilization rates of HCN from ground water may be less than those from surface water. Other processes that tie up cyanide, such as sorption and complexation, may be much more important in limiting the mobility of cyanide in ground water than in surface water. Reaction of cyanide to ammonia and formate may also be an important process to reduce concentrations of cyanide in ground water.

Cyanide is more mobile in soils with anaerobic conditions. The limit for effective microbial degradation of cyanide was found to be 2 mg/l based on studies of a sewage waste stream (Coburn, 1949). Cyanides and cyanide-yielding compounds such as fertilizers and pesticides

applied to aerobic soils readily degrade (Fuller, 1985). Other factors affecting the mobility of cyanide in soil are clay content, depth of soil, content of iron oxides or other metal oxides, pH, and presence of organic matter. Mobility of cyanides is greatest in soils with high pH and low clay content.

The basic chemical process used in a heap leach mining operation is the complexation of Au and Ag from the ore with a sodium cyanide solution. One of two processes, carbon adsorption or zinc precipitation, can be used to recover the precious metals from the pregnant solution.

Neutralization, or a rinsing of the ore heaps, is used to reduce the levels of cyanide remaining in heaps after the ore is spent. Various western states require that the rinsing procedure continue until the cyanide concentration is reduced to a specified level or a certain pH is obtained. The final cyanide concentrations specified by states using free cyanide analyses ranges from 0.2 to 5 mg/l, and from 0.01 mg/l to 100 mg/l in states using total cyanide analyses. Although little data is available, sampling of heaps after the rinsing procedure is completed generally shows less than 10 mg/kg of free cyanide remaining in the heaps. Subsequent sampling shows a decrease of cyanide with time.

A variety of methods are used to destroy cyanide in process solution either during operation or upon closure, and rinsing solution used to neutralize the spent ore heaps. Treatment processes that are, or may be, used at leaching operations are natural degradation, alkaline chlorination, hydrogen peroxide, Inco process, and biological treatment.

Heap leach mining wastes contain free cyanide ( $\text{HCN}$  and  $\text{CN}^-$ ), metal cyanide complexes, and salts of metal cyanide complexes. The amount of free cyanide in these wastes is dependent upon the rate of volatilization of  $\text{HCN}$  to the atmosphere. An important control on volatilization is pH; below a pH of 9,  $\text{HCN}$  is predominant over cyanide ion.

Metal cyanide complexes such as iron, copper, zinc, nickel, cobalt, and cadmium, which are the most common at gold and silver operations (Huiatt, 1985), decompose and release cyanide ion at varying rates. Zinc and cadmium complexes, the least stable complexes, readily decompose during the rinsing process as free cyanide decreases. Strong complexes such as iron cyanide complex may remain in the spent ore. Iron cyanide complexes have been found to degrade in solutions exposed to ultraviolet light, but the photochemical effect on the solid species is unknown. Iron, nickel, cobalt, and copper salts of iron complex cyanide ions are very sparingly soluble and release very small amounts of free cyanide in the spent heap pile.

In addition to volatilization directly from the mining wastes, there is a secondary transport process whereby cyanide and any soluble metal cyanide complexes may be leached from the mining wastes and transported into the environment if uncontained. The accidental release of cyanide process solution is also possible. Several chemical and biological processes have the potential to attenuate cyanide when it is released to the environment.

#### CHEMICAL FORMS OF CYANIDE

A large number of organic and inorganic chemical compounds contain cyanide. Cyanide occurs as a cyano group (CN) in the molecular structure of the compound. In solution, the cyanide ion ( $\text{CN}^-$ ) is a negatively charged, diatomic species, which may complex with both inorganic and organic compounds. Since most metals tend to form positive ions, they may readily react with cyanide. The characteristics of cyanides, particularly the high level of stability for some of the metal cyanide complexes, can be explained by its bonding properties. For the purposes of this report, four different forms of cyanide, free cyanides, simple cyanides, complex cyanides, and cyanogenic glycosides (organic compounds containing cyanide) will be discussed below.

### Free Cyanide

Free cyanide in solution is the total concentration of cyanide ion (CN<sup>-</sup>) and dissolved molecular hydrogen cyanide (HCN). Hydrogen cyanide is a colorless gas or liquid with a boiling point of about 25.5 °C (77.9° F). The gas is less dense than air and flammable.

HCN or hydrocyanic acid, a weak acid, has a dissociation constant of  $4.365 \times 10^{-10}$  at 20 °C (68° F) for the hydrolysis reaction between cyanide ion and water:



The relative amounts of CN<sup>-</sup> and HCN as predicted by this relationship are strongly dependent on the pH of the solution (Figure B-1). The concentration of CN<sup>-</sup> and HCN are equal at pH 9.36, the pK (log of the equilibrium constant) of HCN at 20 °C (68° F) (Broderius, 1974). At pH values below 9.36 and at 20° C (68° F), most cyanide exists as molecular HCN; 69.6 percent at pH 9; 95.8 percent at pH 8; and greater than 99 percent at pH 7. In natural waters most of the free cyanide concentration would be in the form of HCN. Since HCN has a high vapor pressure it readily evaporates depending on the solution concentration, temperature, and pH. Higher temperatures and solution concentrations, and lower pH values promote generation of gaseous HCN.

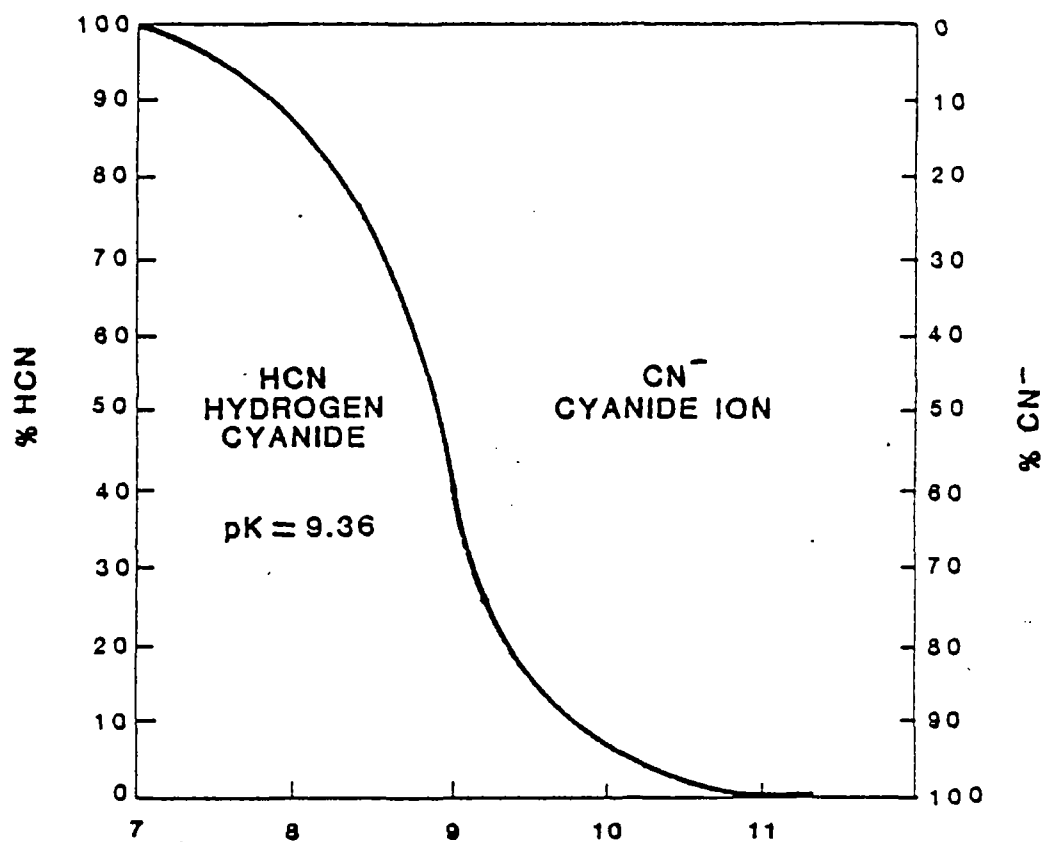
### Simple Cyanides

Simple cyanides consist of an alkali (sodium, potassium) or metal cation and cyanide. They can be represented by the formula A(CN)<sub>x</sub>, where A is an alkali or metal, and x, the valence of A, represents the number of cyano groups present. Solubilities of the simple cyanides are a function of pH and temperature. Soluble compounds (particularly the alkali cyanides) ionize to release cyanide as shown:



Cyanide ions released would undergo hydrolysis as shown in equation (1). An example of a simple cyanide used in heap leaching mining operations is sodium cyanide (NaCN) which would dissolve and readily hydrolyze as shown:

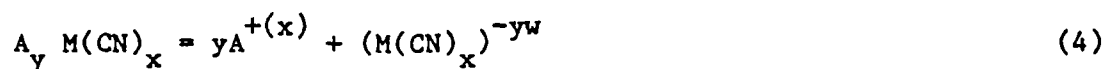
FIGURE B-1  
THE EFFECT OF pH ON DISSOCIATION  
OF HYDROGEN CYANIDE





### Complex Cyanides

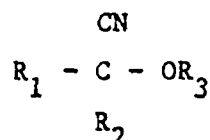
Alkali-metallic cyanides are represented as  $\text{A}_y\text{M}(\text{CN})_x$ , where A is the alkali such as sodium or potassium, y is number of alkalies, M is the heavy metal (ferrous or ferric iron, gold, copper or others), and x is the number of cyano groups. The valence of the alkali (A) taken y times plus the valence of the metal (M) is the value of x. Soluble alkali-metallic cyanides dissociate to release the metal cyanide complex ion,  $(\text{M}(\text{CN})_x)^{-yw}$ , by the reaction:



where w is the oxidation state of A in the original alkali-metallic cyanide compound. The metal cyanide complex ion released may undergo further dissociation and release cyanide ion. Another type of compound with a similar formula is the complex ferro or ferric cyanide salts, where A and M would be a heavy metal and either  $\text{Fe}^{2+}$  (ferrous) or  $\text{Fe}^{3+}$  (ferric), respectively. Some examples of metal cyanide complex ions which may be found in process solutions of heap leach mining operations are  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Cu}(\text{CN})_2^-$ , and  $\text{Zn}(\text{CN})_4^{2-}$ .

### Cyanogenic Glycosides

Organic compounds yielding cyanide are introduced naturally into the environment, particularly the soil. One of the most common natural sources is from plants. A large number of plants (800 species) naturally synthesize cyanogenic glycosides (Knowles, 1976). The general formula is:



where  $\text{R}_1$  = an alkyl or aryl group

$\text{R}_2$  = a hydrogen atom or methyl group

$\text{R}_3$  = usually, D-glucose.

One of the best known cyanogenic glycosides, called amygdalin, occurs in seeds and leaves of many members of the Rosaceae (rose) family (Kingsbury, 1964). Many common vegetables also contain cyanogenic glycosides such as maize, millet, field bean, kidney bean, sweet potato, and lettuce (Oke, 1969). Generally, the glycoside is harmless, but becomes toxic only when in vivo conditions permit hydrolysis of the compound to liberate hydrogen cyanide (refer to Appendix C for a discussion of toxicity).

## ANALYTICAL METHODS

Standard methods for measuring cyanide that are most relevant to the mining industry are described below. These methods include total cyanide, free cyanide, weak acid dissociable cyanide, and cyanide amenable to chlorination. Several problems associated with the analytical methods are also presented.

### Methods for Water Samples

#### Total Cyanide

The acid reflux/distillation method measures the free cyanide and the cyanide contained in complex iron cyanides, weakly acid dissociable cyanide, and most inorganic complex cyanides except gold, cobalt, and some of the platinum metals. The ASTM method (1981) uses a catalytic agent to facilitate the breakdown of the metal cyanide complexes. The hydrogen cyanide liberated by the distillation is collected in an alkaline absorbing solution and can be measured by titration, colorimetry, or specific ion electrode. The lower limit of detection for the three methods are 1.0, 0.03, and 0.03 mg/l, respectively.

Modifications to the ASTM method to eliminate interferences caused by thiocyanate have been developed. In the acid distillation technique, decomposition agents such as hydrochloric acid/hydroxylamine, tartaric acid, or phosphoric acid (Knechtel and Conn, 1981; Huiatt et al., 1983) are used.

The EPA procedures were last revised in 1984 as Method 335.2 (STORET No. 00720). This method is either a titrimetric or a spectrophotometric analytical procedure similar to ASTM. Single laboratory precision is reported as 85 percent and 102 percent recovery at 0.28 and 0.62 mg/l CN, respectively. These recoveries were apparently reported for water samples.

#### Free Cyanide

The methods for determining free cyanide include solvent extraction or sparging the HCN from solution and collecting it for later measurements (Broderius, 1975, Montgomery et al., 1969; Schneider and Freund, 1962).

#### Weak Acid Dissociable Cyanides

The method accepted by ASTM as a standard procedure for determining weak acid dissociable cyanides is called Method C, a variation of one proposed by Roberts and Jackson (1971). The reagents used in the distilling flask are acetic acid-sodium acetate solution buffered at pH 4.5 and zinc acetate. Gonter (1975) reported that cyanide was totally recovered from cadmium, copper, nickel, silver, and zinc complexes. Test work reported by Conn (1981) suggests that some (two percent) breakdown of ferrocyanide could occur. No interference occurs in this method by the presence of thiocyanate.

#### Cyanide Amenable to Chlorination

Cyanide amenable to chlorination is the difference between total cyanide measurements before and an alkaline chlorination treatment. Chlorination treatment oxidizes cyanide, HCN, cyanide from weakly dissociated and moderately strong metal complexes, and thiocyanate, but does break down the iron cyanide complexes or other stable complexes. Refer to the section entitled, Complexation with Metallic Ions for the stabilities of metal cyanide complexes. The sample is separated into two portions; one is analyzed for total cyanide and the other is analyzed for total cyanide after a treatment with sodium hypochlorite at an alkaline pH for one hour. EPA uses Method 335.1 (STORET No. 00722) to determine cyanide amenable to chlorination.



### Methods for Solid Samples

EPA Method 9010 (U.S. Environmental Protection Agency, 1982) may be used to analyze for total and chlorine amenable cyanides in solid wastes or leachate. A draft testing method has just been released by EPA to determine whether a waste is hazardous due to cyanide reactivity (U.S. Environmental Protection Agency, 1986). The memo stated that on an interim basis wastes releasing more than 250 mg HCN/kg waste should be regulated as hazardous waste. Other methods for cyanide analysis in environmental samples are currently being tested. The literature shows that particular methods are suited to specific types of samples depending on the sample composition. Hendrix et al. (1985) has developed a method producing reproducible results suitable for tailings samples. After drying and thorough mixing, 5 grams of sample were mixed with 20 millimeters of 1 N NaOH and about 200 milligrams of  $\text{PbCO}_3$ , and filtered into a distillation flask. The filtrate was analyzed for total cyanide by the ASTM method. Free cyanide was analyzed directly without the caustic filtration pretreatment. J.L. Hendrix (University of Nevada at Reno, personal communication, 1986) is also developing analytical methods to determine the amounts of specific metal cyanide complexes present.

Several different leachate solutions, deionized water, 1 N  $\text{KNO}_3$  in water, and 1.25 N NaOH in water, were tested on samples from heap leach piles by Ray (1985). The procedure for analysis consisted of leaching a 20 gram sample in 100 millimeters of leachate solution for 24 hours in the dark. After leaching, the sample was filtered (Whatman GF/C or equivalent) until the final volume was 100 millimeters. The leachate was then analyzed by the distillation/destruction method with a colorimetric finish. The results for direct analysis (0.5 gram sample in distillation flask) and the three leachate methods are presented in Table B-1. Only the NaOH solution solubilized cyanide at a level similar to that found in the direct analysis. The data also show that reproducibility of results is greatly increased with the larger sample sizes.

Snodgrass, 1985). The total cyanide concentration of the iron cyanide complex solution was 10 mg/l after 15 days. The decay rate of the nickel cyanide complex solution was so slow that the concentration had not decreased to less than 30 mg/l even after nine days.

#### Photochemical Degradation

The iron cyanide complexes,  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$ , in water produce free HCN from photochemical degradation by sunlight (Broderius and Smith, 1980). The lower the concentration of the iron complex ions, the faster the rate of photodegradation. The amount of HCN formed will increase with increasing concentration of the photolabile iron cyanide. The maximum amount of total cyanide (complexed cyanide) converted to free cyanide was 85 percent and 49 percent for  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$ , respectively. Photodegradation rates decrease rapidly with depth in natural water systems. The ultraviolet radiation from the midday sun on a Minnesota lake during summer accelerated the decomposition of ferricyanide to a resultant half life of 20 minutes (Broderius, 1973). During the fall the half-life increased to 50 minutes. Simovic et al. (1985) research with degradation of metal cyanide solutions showed that of the variables, temperature, aeration, and presence of ultraviolet light, ultraviolet light had the largest effect on the iron cyanide solution. The results of tests by both Moggi et al. (1966) and Kelada et al. (1985) showed that cobalt III cyanide complex also is broken down by ultraviolet radiation.

#### Cyanogenic Glycosides Transformation and Degradation Processes

Cyanide may be released from cyanogenic glycosides subjected to hydrolysis in vitro by dilute mineral acids or in vivo by enzymes. One of the best known cyanogenic glycosides, amygdalin, occurs in the Rosaceae (rose) family. The hydrolysis of amygdalin is shown in Figure B-2. The HCN released from cyanogenic glycosides may undergo any of transformation or degradation processes described above for free cyanide.

TABLE B-1  
COMPARISON OF LEACHING METHODS  
FOR TOTAL CYANIDE DETERMINATION IN SOLID SAMPLES

Run #	Direct Analysis <sup>a/</sup> (mg/kg)	Leaching Method		
		DI Water (mg/kg)	1 N KNO <sub>3</sub> (mg/kg)	1.25 N NaOH (mg/kg)
1	45.2	0.8	0.6	142
2	125	0.6	0.4	47.9
3	77.5	<0.2	<0.2	43.2
4	57.3	<0.2	<0.2	109
5	179	0.6	<0.2	106
6	114	0.2	0.4	91.9
7	129			116
8	88.1			114
9	98.3			
10	170			
11	196			
12	104			
13	114			
14	59.9			
15	65.1			
Mean	108	0.4	0.2	96.2 <sup>b/</sup>
+ 1 S.D.	45.9	0.3	0.3	34.3

a/ Analysis of 0.5 g sample.

b/ If values from runs #2 and #3 are omitted, the mean is  $113 \pm 16.5$  (+ 1 S.D.).

Source: Modified from Ray, 1985.

Several other examples which illustrate the diversity of methods used for solid samples are described below:

Engelhardt (1985) and Milligan (1985a) - 200-gram split of spent heap material (reprocessed tailings) was agitated for one hour with 200 milliliters of distilled water; after filtering, the pH was adjusted to 12.0 with sodium hydroxide, and then analyzed for free and total cyanide.

Stotts (1985) - 25 grams of spent heap material was placed in 50 millimeters of 20 percent NaOH solution and allowed to mix until delivered to the laboratory which was 12 to 24 hours later; solution was then analyzed for free cyanide.

The actual data from these examples on cyanide concentrations in spent heap leach piles is presented in the section, Cyanide in Spent Leach Piles.

#### Problems Associated with Analyses.

Problems can occur with sample preservation for water samples containing solids. A clear, filtered sample preserved by the addition of sodium hydroxide to a pH of 12 and stored in the dark at 4° C (40° F) will be stable for at least two weeks (Huiatt et al., 1983). There is, however, no guaranteed method of preservation when solids are present (Conn, 1981). Samples with solids can be filtered and preserved or analyzed immediately. If a sample is known to contain sulfides, these should be removed by precipitation with lead carbonate before raising the pH for preservation.

There are many potential sources of interference in analytical determinations for cyanide including sulfides, oxidizing materials, thiocyanates, nitrate-nitrite, carbonate-bicarbonate, metal cations, aldehydes, fatty acids, and potential cyanide-forming materials. ASTM (1981) states that it is beyond their scope to describe procedures for overcoming all the interferences that may be encountered.

Some other problems that have been noted in the literature is that the cyanide ion-selective electrode can be attacked by cyanide solutions which causes inaccurate results (Frant, et al., 1972). Sulfide also causes problems by deactivating the surface of the electrode.

## ENVIRONMENTAL FATE OF CYANIDE

Cyanide is a very reactive and relatively short-lived contaminant unlike many pollutants which may enter the environment. Research work on natural destructive mechanisms and rate of degradation for cyanide in the environment has begun recently. This section will focus on the transformation and degradation process for free cyanide, simple cyanides, complex cyanides, and cyanogenic glycosides thought to be most significant to the environmental aspects of a mining operation, and will conclude with a discussion of the factors influencing the mobility of cyanide in surface water, ground water, and soils.

### Free Cyanide Transformation and Degradation Processes

#### Volatilization

The most important mechanism in the natural degradation of cyanide in water is recognized as volatilization of HCN (Simovic et al., 1985). As discussed above, molecular HCN is the dominant species of cyanide at pH values below 9.36. Since molecular HCN has a high vapor pressure, it can readily be volatilized to the atmosphere. Volatilization of HCN was found to be influenced by pH, temperature, interfacial surface area, and concentration (Dodge and Zabbon, 1952). Stripping coefficients were greatly reduced in stagnant solutions compared to agitated solutions since the process became dependent on molecular diffusion. The Chester Engineers (1977) studied dilute cyanide solutions in the range of 0.1 to 0.5 mg/l. The volatilization rate was  $0.04 \text{ kg-mole/hr-m}^2\text{-atm}$  ( $0.009 \text{ lb-mole/hr-ft}^2\text{-atm}$ ) in still waters, which is equivalent to the volatilization of 0.23 milligram  $\text{CN/m}^2\text{-hr}$  ( $0.021 \text{ milligram CN/ft}^2\text{-hr}$ ) from a 0.5 mg/l cyanide solution at room temperature. Volatilization rates in agitated waters were up to three times as fast.

Palaty and Horokova-Jakubu (1959) examined several factors, pH, temperature, solution depth, presence or absence of aeration and the rate of aeration, which affect HCN removal. The experiment involved HCN removal from an unbuffered, synthetic simple cyanide solution (KCN) at relatively low concentrations (10-50 mg/l CN) over a period of 11 days. The HCN removal rate increased with decreasing pH down to 5; an order of magnitude difference in the rates of HCN removal existed between aerated and nonaerated solutions; and a temperature increase of 10° C (50° F) from 0.8 to 11° C (33 to 52° F) caused the HCN removal rate to increase by greater than 40 percent.

Broderius (1977) conducted experiments on the volatilization of cyanide from natural water using concentrations of cyanide from 25 to 200 ug/l. The concentrations of cyanide in the water were measured during a 6-hour period, from which half lives of 8.8 to 55.5 hours were calculated for HCN disappearance. Disappearance of HCN became negligible when the samples were sealed and closed off from the atmosphere.

Simovic et al. (1985) studied the rate of cyanide degradation from a NaCN solution as well as from solutions containing a single metal cyanide complex and mixtures of metal cyanide complexes. Data from the solutions containing metal cyanide complexes and metal complex mixtures will be presented in the following section, Complex Cyanide Transformation and Degradation Processes. The initial total cyanide concentration for the NaCN solution at 4° C (40° F) was 200 mg/l. Air was bubbled through the solution and the solution was exposed to ultra-violet light. A phosphate buffer was added to maintain a constant pH of 7.0. The total cyanide concentration decayed to less than 1 mg/l after about 230 hours (9.6 days). The decay rate was initially much higher during the first 80 hours (2.1 mg/l per hour).

#### Reaction of Cyanide to Formate and Ammonia

Cyanide in water reacts to form ammonia and formate ions. Reaction products from an acidic cyanide solution are formic acid and ammonium salts and from a basic solution are formate salts and volatile ammonia. Reaction of HCN in strongly acidic solutions (pH <1) was

found to proceed with half-lives ranging from 10 to 1000 hours (Kreibler and McNally, 1929). The rate constants for the reaction of cyanide ion under alkaline conditions range from  $2 \times 10^{-8} \text{ sec}^{-1}$  to  $2 \times 10^{-6} \text{ sec}^{-1}$  at temperatures between 33 and 65° C (91 and 150° F) (Wiegand and Tremelling, 1972).

#### Oxidation

Direct oxidation of cyanide to cyanate ( $\text{CNO}^-$ ) requires mineralogical, biochemical or photochemical catalysis. The reaction is:



Another route for oxidation is by hydrolysis to HCN and subsequent oxidation:



In water cyanic acid (HCNO) can hydrolyze to produce cyanate ( $\text{CNO}^-$ ). Hendrickson and Daignault (1973) have shown that cyanic acid can be hydrolyzed to carbon dioxide and ammonia. The hydrolysis reaction is:



This reaction is pH dependent, and occurs at a pH up to 8.5, but is greatly accelerated at lower pH values. Further oxidation of ammonia would form nitrate.

According to Schmidt et al. (1981) oxidation processes may have accounted for about 11 percent of the decrease in cyanide from a relatively shallow holding pond for mill cyanide process solutions over a six month period during the warm season.

#### Complexation with Metallic Ions

Some 28 elements are capable of forming 72 possible metal cyanide complexes (Ford-Smith, 1964). The relative stabilities of some of the common cyanide complexes in water are given in Table B-2. The stronger or more stable the cyanide complex, the less free cyanide ion required to maintain it in solution and the less readily it dissociates to yield cyanide ions.

TABLE B-2

RELATIVE STABILITIES OF SOME CYANIDE COMPOUNDS  
AND COMPLEXES IN WATER

<u>Term</u>	<u>Examples of Cyanides in Processing Solutions</u>
1. Free Cyanide	$\text{CN}^-$ , HCN
2. Simple Compounds	
a) readily soluble	NaCN, KCN, $\text{Ca}(\text{CN})_2$ , $\text{Hg}(\text{CN})_2$
b) relatively insoluble	$\text{Zn}(\text{CN})_2$ , CuCN, $\text{Ni}(\text{CN})_2$ , AgCN
3. Weak Complexes	$\text{Zn}(\text{CN})_4^{2-}$ , $\text{Cd}(\text{CN})_3^-$ , $\text{Cd}(\text{CN})_4^{2-}$
4. Moderately Strong Complexes	$\text{Cu}(\text{CN})_2^-$ , $\text{Cu}(\text{CN})_3^{2-}$ , $\text{Ni}(\text{CN})_4^{2-}$ , $\text{Ag}(\text{CN})_2^-$
5. Strong Complexes	$\text{Fe}(\text{CN})_6^{4-}$ , $\text{Co}(\text{CN})_6^{4-}$ , $\text{Au}(\text{CN})_2^-$

Source: Adapted from Scott and Ingles, 1981.



The dissociation of a complex cyanide ion involves a number of intermediate reactions, some of which may be rate limiting steps. At a given temperature, pH and the concentration of the complex ion influence the dissociation rate (Broderius, 1973). Rates of dissociation generally increase with either decreasing pH or decreasing total cyanide concentration. Dissociation of metal cyanide complex ions will be discussed further in the section, Dissociation of Metal Cyanide Complex Ions.

#### Biological Degradation

Biological destruction appears to be a significant means of reducing cyanide concentration. Numerous studies have shown that many bacteria, fungi, and algae are capable of utilizing cyanides, converting cyanide to carbon dioxide and ammonia. Biochemical degradation of cyanide may occur under both aerobic and anaerobic conditions over a wide pH range (Towill et al., 1978). Under aerobic conditions cyanide decomposes to carbon dioxide and ammonia biochemically as shown by either in equation (5) or (6), and equation (7). Cyanide decomposes to thiocyanate ( $\text{SCN}^-$ ) under anaerobic conditions as shown:



Thiocyanate may hydrolyze to produce hydrogen sulfide, carbon dioxide and ammonia. Schmidt et al. (1981) suggests the general pathways for anaerobic decomposition are as follows:



Higher plants and animals have the capacity to metabolize sublethal doses of administered cyanide to thiocyanate (Towill et al., 1978). Activated sludge treatment can result in virtually complete removal of cyanide (Ludzack and Schaffer, 1962; Kostenbalder and Flecksteiner, 1969), but Raef et al., (1977b) thought that most of the loss of cyanide in such systems is due to stripping (volatilization).

### Conversion to Thiocyanate

If sulfide ( $S^{2-}$ ) or thiosulfate ( $S_2O_3^{2-}$ ) is present in the environment, cyanide can react to form thiocyanate ( $SCN^-$ ). This chemical process would occur where sulfide minerals are oxidizing. Metal thiocyanate complexes may be formed but the formation potential for metal cyanide complexes is much greater than for metal thiocyanate complexes. If free cyanide is absent, then metal thiocyanate complexes will form. Many of metal thiocyanate complexes found in ore processing solutions are insoluble. This process may play a role in removing some cyanide and metals from solution.

### Sorption

Sorption of free cyanide, as well as complexed cyanides, to clays (Cruz et al, 1974; Schenk and Wilke, 1984), soils (Alesfi and Fuller, 1976; Fuller, 1985), sludge (Raef et al, 1977a) and plant debris (Schenk and Wilke, 1984) occurs to a small extent.

### Simple Cyanide Transformation and Degradation Process

The relative solubility of several simple cyanides is shown in Table B-2. The soluble compounds can readily release free cyanide, which may be subjected to the degradation processes described above. However,  $Zn(CN)_2$ ,  $CaCN$ ,  $Ni(CN)_2$ , and  $AgCN$  are relatively insoluble in water.

### Complex Cyanide Transformation and Degradation Processes

#### Solubilities of Complex Cyanides Salts

The solubilities of iron cyanide salts are listed in Table B-3. Most of these compounds are relatively insoluble. If an iron cyanide salt dissolves, the products are an alkali or heavy metal ion and either a ferrocyanide or ferricyanide complex, which are strong complexes. The dissociation of metal cyanide complexes such as ferrocyanide and ferricyanide is discussed below.

TABLE B-3

## SOLUBILITIES OF FERROCYANIDE AND FERRICYANIDE SALTS

<u>Name</u>	<u>Formula</u>	<u>Solubility (g/l)<sup>a/</sup></u>
Ammonium Ferricyanide	$(\text{NH}_4)_3\text{Fe}(\text{CN})_6$	very soluble
Ammonium Ferrocyanide	$(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	soluble
Barium Ferrocyanide	$\text{Ba}_2\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$	1.7 (15°C)
Cadmium Ferrocyanide	$\text{Cd}_2\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$	insoluble
Calcium Ferrocyanide	$\text{Ca}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$	868 (25°C)
Cobalt Ferricyanide	$\text{Co}_3(\text{Fe}(\text{CN})_6)_2$	insoluble
Cobalt Ferrocyanide	$\text{Co}_2\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$	insoluble
Copper (I) Ferricyanide	$\text{Cu}_3\text{Fe}(\text{CN})_6$	insoluble
Copper (II) Ferricyanide	$\text{Cu}_3(\text{Fe}(\text{CN})_6)_2 \cdot 14\text{H}_2\text{O}$	insoluble
Copper (II) Ferrocyanide	$\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$	insoluble
Iron (II) Ferricyanide	$\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$	insoluble
Iron (III) Ferricyanide	$\text{Fe Fe}(\text{CN})_6$	--
Iron (II) Ferrocyanide	$\text{Fe}_2 \text{Fe}(\text{CN})_6$	insoluble
Iron (III) Ferrocyanide	$\text{Fe}_4 (\text{Fe}(\text{CN})_6)_3$	$2.5 \times 10^{-4}$ b/
Lead Ferricyanide	$\text{Pb}_3 (\text{Fe}(\text{CN})_6)_2 \cdot 5\text{H}_2\text{O}$	slightly soluble
Magnesium Ferrocyanide	$\text{Mg}_2\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$	330g
Manganese (II) Ferrocyanide	$\text{Mn}_2\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$	insoluble
Nickel Ferrocyanide	$\text{Ni}_2\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$	insoluble
Potassium Ferricyanide	$\text{K}_3\text{Fe}(\text{CN})_6$	330 (4°C)
Potassium Ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	278 (12°C)
Silver Ferricyanide	$\text{Ag}_3\text{Fe}(\text{CN})_6$	0.00066 (20°C)
Silver Ferrocyanide	$\text{Ag}_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$	insoluble

(Continued)

TABLE B-3 (Continued)

<u>Name</u>	<u>Formula</u>	<u>Solubility (g/l)<sup>a/</sup></u>
Sodium Ferricyanide	$\text{Na}_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$	189 (0°C)
Sodium Ferrocyanide	$\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$	318.5 (20°C)
Strontium Ferrocyanide	$\text{Sr}_2\text{Fe}(\text{CN})_6 \cdot 15\text{H}_2\text{O}$	500
Thallium Ferrocyanide	$\text{Tl}_4\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$	3.7 (18°C)
Tin (II) Ferricyanide	$\text{Sn}_3 (\text{Fe}(\text{CN})_6)_2$	insoluble
Tin (II) Ferrocyanide	$\text{Sn}_2\text{Fe}(\text{CN})_6$	insoluble
Tin (IV) Ferrocyanide	$\text{SnFe}(\text{CN})_6$	insoluble
Zinc Ferrocyanide	$\text{Zn}_2 \text{Fe}(\text{CN})_6$	insoluble
Zinc Ferricyanide	$\text{Zn}_2 (\text{Fe}(\text{CN})_6)_2$	$2.6 \times 10^{-5\text{b/}}$
Zinc Ferrocyanide	$\text{Zn}_3 (\text{Fe}(\text{CN})_6)_2$	$2.2 \times 10^{-5\text{b/}}$

Source: Weast, 1969

a/ Source unless otherwise noted is from Weast , 1969.

b/ Source: Mezey and Neuendorf, 1981.

### Dissociation of Metal Cyanide Complex Ions

A stability constant is a measure of the affinity or tightness of the binding of the complex between the cyanide radical and a metal. The reaction between a metal ion and cyanide to form a metal cyanide complex is



where M = metal with valence y; and

x = number of cyanide groups in the complex.

The stability constant or the inverse of the stability constant, the dissociation constant, is expressed as follows:

$$K_s = \frac{[M(CN)_x^{(x-y)-}]}{[M^{y+}][CN^{x-}]} = \frac{1}{K_d} \quad (12)$$

where  $K_s$  = stability constant;

$K_d$  = dissociation constant; and

[ ] = concentration units in moles per liter.

The values for the stability constants for metal cyanide complex ions are shown in Table B-4.

In a solution containing different metals where more than one complex can form, a cumulative or gross constant,  $B_n$ , is used to describe the reactions between the metals and cyanide:



The cumulative constant,  $B_n$ , is expressed as follows:

$$B_n = \frac{[M(CN)_n]}{[M][CN]^n} \quad (14)$$

where the concentration units, [ ], are moles per liter.

The cumulative constant for specific metals can be quantified by the results of potentiometric titrations conducted both in the presence of and absence of the metal. Cumulative constants for individual metal ions are presented in Table B-5. The  $B_n$  values indicate the relative

TABLE B-4

## STABILITY CONSTANTS OF METAL-CYANIDE COMPLEX IONS

<u>COMPLEX ION</u>	<u>STABILITY CONSTANT<sup>a/</sup></u>
$\text{Cr}(\text{CN})_6^{3-}$	$10^{33}$
$\text{Cr}(\text{CN})_6^{4-}$	$10^{21}$
$\text{Fe}(\text{CN})_6^{4-}$	$10^{35.4}$
$\text{Fe}(\text{CN})_6^{4-}$	$10^{47}$ b/
$\text{Co}(\text{CN})_6^{4-}$	$10^{50}$
$\text{Ni}(\text{CN})_4^{2-}$	$10^{30}$
$\text{Pd}(\text{CN})_4^{2-}$	$10^{42}$
$\text{Pt}(\text{CN})_4^{2-}$	$10^{40}$
$\text{Cu}(\text{CN})_2^{-}$	$10^{23.9}$
$\text{Cu}(\text{CN})_3^{2-}$	$10^{29.2}$
$\text{Cu}(\text{CN})_4^{2-}$	$10^{30.7}$
$\text{Ag}(\text{CN})_3^{2-}$	$10^{20.4}$
$\text{Ag}(\text{CN})_3^{2-}$	$10^{21.9}$
$\text{Au}(\text{CN})_2^{-}$	$10^{37}$
$\text{Au}(\text{CN})_4^{-}$	$10^{85}$ (estimate)
$\text{Zn}(\text{CN})_4^{2-}$	$10^{21}$
$\text{Cd}(\text{CN})_4^{2-}$	$10^{19}$
$\text{Hg}(\text{CN})_4^{2-}$	$10^{39}$

a/ Source unless otherwise noted is from Sharpe, 1976.

b/ Source: Broderius, 1973.

TABLE B-5  
CUMULATIVE CONSTANTS,  $B_n$ , FOR VARIOUS METALS  
FOUND IN PRECIOUS METAL ORES

<u>Metal</u>	<u>Valence</u>	<u><math>a_n</math></u>	<u>Log (10) of <math>B_n</math></u>	<u>Log (10) of [CN]</u>
Cadmium	+2	4	16.85	-1.6
Cobalt	+2	6	19.09	-1.5
Cobalt	+3	6	64	-9.0
Copper	+1	4	27.3	-4.3
Gold	+1	2	47.5	-18.6
Gold	+3	4	56	-11.4
Lead	+2	4	10.3	0
Mercury	+2	4	41.4	-7.8
Nickel	+2	4	31	-5.2
Silver	+1	4	21.1	-2.7
Zinc	+2	4	16.9	-1.7

$a_n$  = number of cyanide molecules in the metal-cyanide complex.

Source: Milligan, 1985b.

strength of the metal cyanide complex. To get an idea of how much cyanide in solution is needed to form a specific metal cyanide complex, Milligan (1985b) assumed a cyanide-metal complex to metal ratio equal to  $2.0 \times 10^{10}$ , and then solved for free cyanide content. Lead, for example, requires a free cyanide content of 1 mole per liter, while all other metals (Table B-5) would be dissolved and leached from the ore when mixed with smaller quantities of free cyanide. Certain minerals containing these metals in the ore may be more stable than the cyanide complex, and therefore the metal cyanide complex may not form.

The equations for cumulative constant or dissociation constant can be combined with the equation for dissociation of hydrogen cyanide to calculate equilibrium hydrogen cyanide concentration at given pH values and initial concentrations of the metal complex. A decrease in pH accelerates the reaction as does a decrease of initial concentration.

The rate of dissociation of metal cyanide complexes is also an important factor. The dissociation of a synthetic solution of single metal cyanide complexes (Cu, Zn, Ni, and Fe) was studied by Simovic et al. (1985). The test solutions (initially 200 mg/l total cyanide) were aerated, illuminated with ultraviolet light, and maintained at pH 7 (phosphate buffer). There was an initial rapid decrease in the total cyanide concentrations within the first 48 to 72 hours, which was attributed to volatilization of hydrogen cyanide. The total cyanide concentration continued to decline, but at a slower rate. The metal cyanide complex decay coefficient was determined for the two different temperatures tested (Table B-6). The half life for each metal cyanide complex was calculated from this data. Zinc cyanide complex had the fastest decay rate, followed by copper, iron, and nickel complexes. Only the decay rate of iron cyanide complex was affected by ultraviolet light (which is discussed in the next section). Other data from these studies, showed that residual total cyanide concentrations decreased to less than 1 mg/l within four days for the zinc cyanide complex solution and within 12 days for the copper cyanide complex solution (Simovic and



TABLE B-6

DEGRADATION OF METAL CYANIDE COMPLEXES IN  
PHOSPHATE BUFFER AT pH 7<sup>a/</sup>

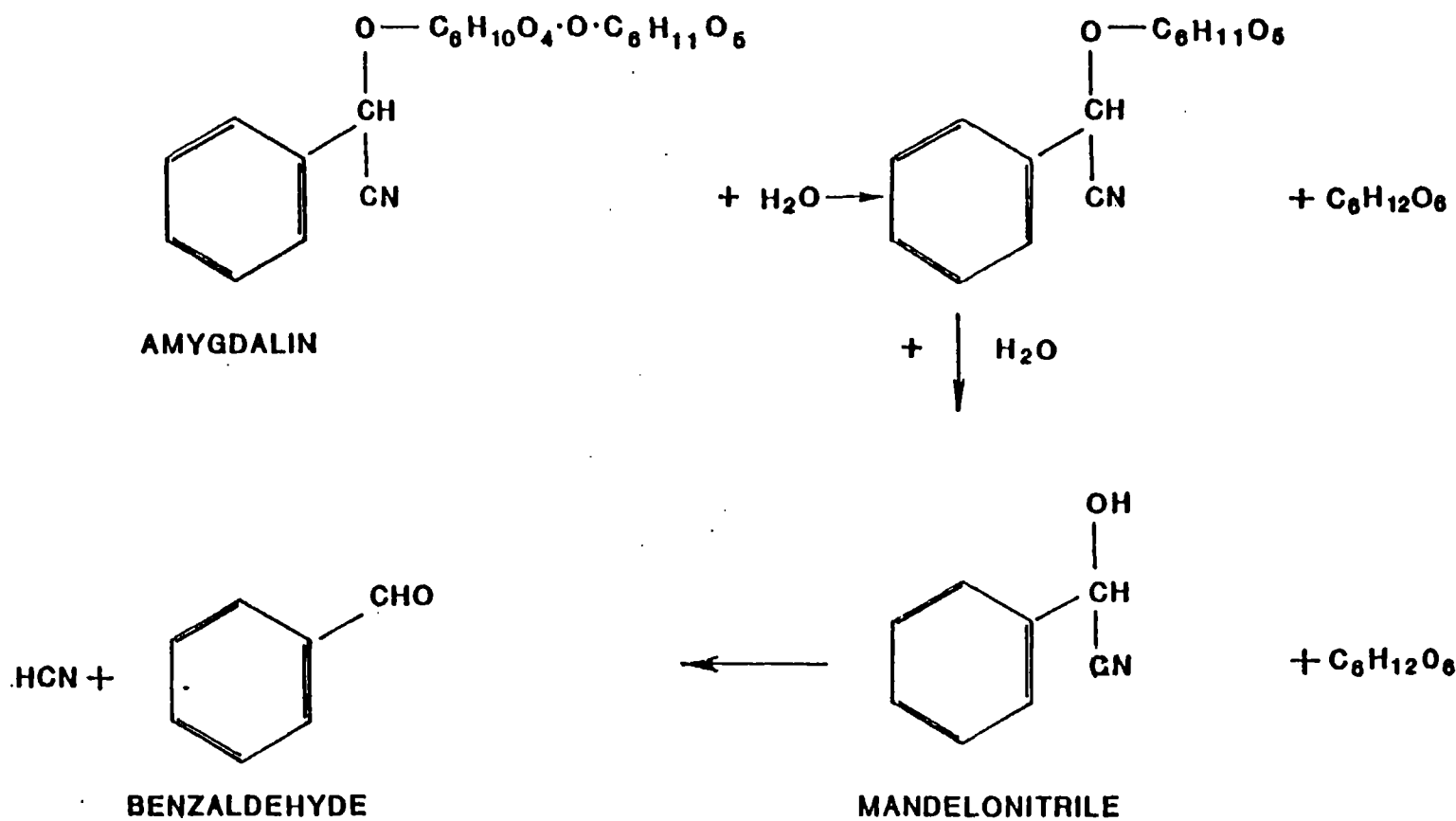
	$k_1 \times 10^2$ (4 °C) (hr <sup>-1</sup> )	$t_{1/2}^{b/}$ (4 °C) (days)	$k_1 \times 10^2$ (20 °C) (hr <sup>-1</sup> )	$t_{1/2}^{b/}$ (20 °C) (days)
Zn(CN) <sub>4</sub> <sup>2-</sup>	1.78	1.6	4.49	0.64
Cu(CN) <sub>3</sub> <sup>2-</sup>	0.29	9.9	0.75	3.8
Fe(CN) <sub>6</sub> <sup>3-</sup>	0.14	20.6	0.47	6.1
Ni(CN) <sub>4</sub> <sup>2-</sup>	0.04	72.1	0.09	32.0

a/ Initial concentration is 200 mg/l. Adapted and modified from Simovic et al., 1985.

b/ Half-lives were calculated from the rate constants (Versar Inc., 1986).

FIGURE B - 2

THE HYDROLYSIS OF A CYANOGENIC GLYCOSIDE, AMYGDALIN



### Mobility of Cyanide in Surface Water

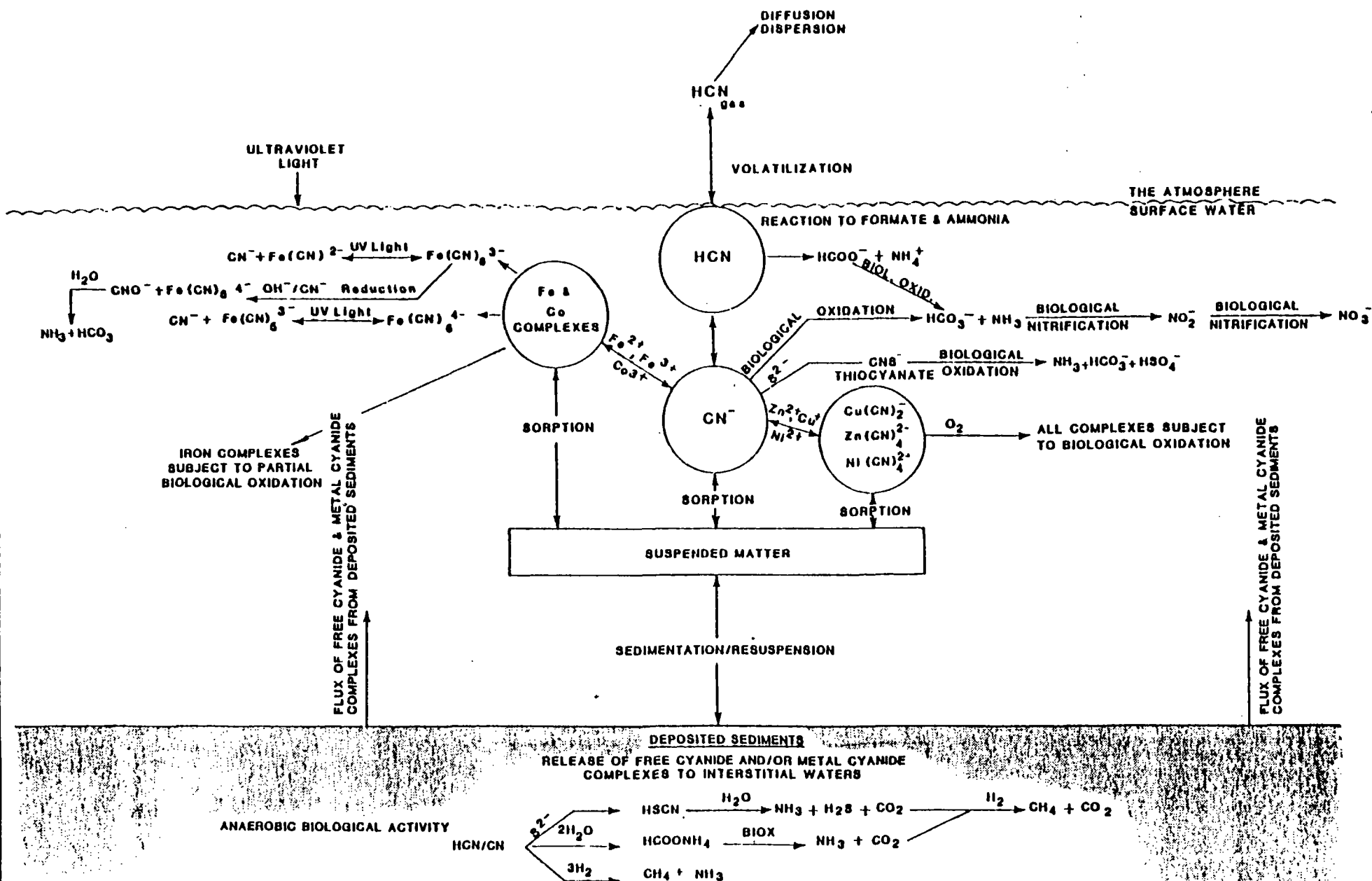
Figure B-3 summarizes cyanide reactions in surface water. The mobility of cyanide in surface water will be dependent on a large number of factors, including pH, temperature, concentration and type of metals and resulting metal cyanide complexes, properties of the water body (depth, surface area, amount of turbulence or aeration), presence of ultraviolet light, and quantities and forms of transported organic and inorganic suspended matter, and interchange with sediment. The different mechanisms for cyanide degradation have been discussed above; each location will have its own set of factors which may tend to release or immobilize cyanide. Generally, free cyanide ion will be more mobile in waters with higher pH, lower temperature, lower levels of metals, organic and inorganic suspended matter, and little interaction with sediment. The properties of a water body that would promote higher mobility of cyanide are stagnant, deep conditions with little surface area. Cyanide will more readily volatilize in highly aerated waters with lower pH's. Free cyanide will be less mobile in waters where there are higher concentrations of metals, sulfide, and organic and inorganic matter. If iron or cobalt complexes are present, then the presence of ultraviolet light may be a factor in increasing the mobility of cyanide.

No predictive models have been developed for the mobility of cyanide in streams. However, several models have been developed to predict the natural degradation of cyanide in gold mining effluents (refer to the section, Degradation of Cyanide at Heap leach Operations).

### Mobility of Cyanide in Ground Water

The mobility of cyanide in ground water is also dependent on many factors such as pH, temperature, concentration and type of metals present and subsequent formation of metal cyanide complexes, amount of aeration, and interaction with soil or rock particles. Volatilization rates of HCN from ground water are probably reduced compared to surface water. Volatilization, however, may be an important process in the

**FIGURE B-3**  
**CYANIDE REACTIONS IN SURFACE WATER**



SOURCE: MODIFIED AFTER MUDDER, 1985

vadose zone. Several researchers have showed that stripping coefficients for stagnant cyanide solutions were greatly reduced compared to agitated solutions, since the process becomes dependent on molecular diffusion. On the other hand, processes that tend to tie up cyanide such as sorption and complexation may be more important processes for ground water than surface water. Ground water flow is generally much slower than surface water which allows more time for interaction of the water with soil or rock minerals. Reaction of cyanide to ammonia and formate ions may also be an important process to remove cyanide from ground water. The other factors such as pH and temperature are also important and vary in the same way as for surface water; that is cyanide is more mobile at higher pH values and lower temperatures. Iron and cobalt cyanide complexes will not undergo photochemical degradation in ground water; however, if ground water is discharged to surface water this process may become important.

#### Mobility of Cyanide in Soils

The mobility of cyanide in soils is largely dependent on soil clay content, depth of soil, content of hydrous oxides of iron, manganese, aluminum and other metals, pH, presence of aerobic or anaerobic conditions, and presence of soil organic matter (Fuller, 1985). Alesi and Fuller (1976) and Fuller (1985) found cyanide in water as  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{CN}^-$  to be very mobile in soils, whereas cyanide as KCN in natural landfill leachate (which contained metals) was less mobile in soils. During this experiment, the anaerobic state of the soil columns inhibited microbial degradation of cyanide. The limit for effective anaerobic degradation of cyanide was found to be 2 mg/l in studies of a sewage wastestream (Coburn, 1949), which is considerably lower than 100 mg/l used in the experiment. The high clay content soil retained more ferricyanide than the sandier soil of similar pH. Ferricyanide was retained the most in soils having a low pH, which was explained by the clay surface having a high percentage of positive exchange sites. The KCN solution leached most rapidly in the soil having the lowest pH.

Cyanide was retained most by soils having a high concentration of hydrous oxides. Mobility of cyanides is greatest in soil at high pH and low clay content.

Cyanide-yielding compounds rapidly ammonify and nitrify in the same soils under aerobic field conditions (Fuller, 1985). In fact, despite regular use of pesticides and fertilizers containing low levels of cyanides or cyanide-yielding compounds, cyanides do not accumulate in the soil.

Wharf Resources Inc. (1982) conducted tests of effluent from cyanide solutions applied to soil columns containing native soil from the Annie Creek Mine area in the Black Hills, South Dakota (Table B-7). Results from the 150 mg/l total cyanide solution showed that both total and free cyanide were reduced to less than half the concentration of the originally applied solutions during the test and continued to decline over the next 6 weeks.

Research is being conducted by DuPont on soil collected from below heap leach pads at two mining operations (F. DeVries, Dupont Company, personal communication, 1986). Besides describing soil mineralogy, they are conducting two types of tests including 1) stirred reaction with cyanide, and 2) column tests with cyanide. Data from these tests will be incorporated into a model used to predict the mobility of cyanide in soils.

## CYANIDE CHEMISTRY OF HEAP LEACH OPERATIONS

### Cyanidation

In the cyanidation process, precious metals are leached from ores with a cyanide solution. In most mineral leaching operations in the United States, the leaching solution is prepared from sodium cyanide. The sodium cyanide in solution will dissociate to sodium and cyanide ion as discussed above (equation 3). The optimum pH process solution for leaching purposes is 10.3 (Barsky et al., 1962), so cyanide ion remains predominant (refer to Figure B-1). The leaching solution contains sodium cyanide at a concentration of 0.05 percent (equivalent

TABLE B-7

RESULTS OF TESTS WITH CYANIDE SOLUTIONS (in mg/l) ADDED TO  
COLUMNS CONTAINING NATIVE SOIL FROM THE AREA OF ANNIE CREEK MINE, SD<sup>a/</sup>

<u>Test Conditions</u>	<u>Date</u>	<u>Test 4-SS</u> (Nominally 150 mg/l)		<u>Date</u>	<u>Test 5-SS</u> (Nominally 1 mg/l)	
		<u>Free CN</u>	<u>Total CN</u>		<u>Free CN</u>	<u>Total CN</u>
Influent solution	8/16 - 8/19/82	36.5	149	8/25 - 8/27/82	1.0	1.0
Effluent	8/17	4.5	65	8/26	<0.01	0.03
Effluent	8/18	17	46.5	8/27	<0.01	<0.01
Effluent following fresh-water flush	10/4	2.4	29	10/4	<0.05	<0.05

Source: Wharf Resources Inc., 1982.

<sup>a/</sup> Cyanide solutions added to soil columns at about 20 l/min/m<sup>2</sup> (0.5 gal/min/ft<sup>2</sup>) for 3 days.

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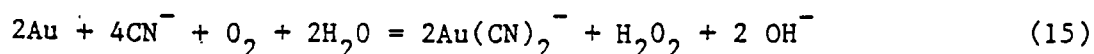
Source: Wharf Resources Inc., 1982.

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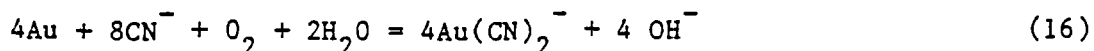


to about 250 mg/l free cyanide) Chamberlain and Pojar (1984). At some operations, the cyanide concentration is much higher (600 to 1000 mg/l) for the first few days of leaching and subsequently drops to approximately 200 mg/l. The rate of dissolution depends on cyanide concentration, oxygen availability, temperature and solution pH. The efficiency of leaching depends on the type of ore. Ore that contains clean, free fine-sized gold particles, little clay content, and no cyanide impurities that may destroy cyanide or inhibit its reaction provides the most efficient leaching situation. Since the reaction is temperature sensitive, the leaching rate of precious metals during colder conditions may be only 70 percent of the leaching rate during summer operating conditions (Milligan, 1985b). Examples of cyanicides are sulfide and ferrous or ferric iron. Details of two example cyanide leaching operations are provided in Appendix A.

The reaction for dissolution of gold and complexation with cyanide is (Heinen et al., 1978):



A lesser amount of gold is solubilized as shown in the Elsner's equation:

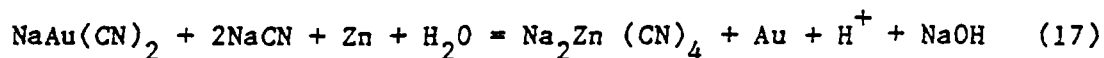


The equations for silver dissolution are similar.

Other metal cyanide complexes may be present in the leaching solution depending on the various metals and their forms in the ore. If the metals in the ore are in the form of compounds less stable than the cyanide complex and the metals are exposed to the leaching solution, then the rate of metal dissolution by cyanide increases directly in proportion to the free cyanide concentration present in the solution. Eventually, a limit is reached at the maximum dissolution rate of the metal cyanide complex; further increases in the free cyanide concentration may have a slight retarding effect on the dissolution rate of the complex (Milligan, 1985b).

The pregnant solution (process solution containing complexed precious metals) is processed through carbon adsorption columns and/or zinc precipitation units in order to recover the gold and silver. In the carbon process the metal cyanide complexes adsorb to the carbon surface. When the carbon columns reach a certain loading capacity, the metals are stripped from the carbon with an alcohol-caustic-cyanide solution. The gold and silver from this solution is removed by electrowinning.

Alternatively, zinc dust is added to the pregnant solution to precipitate the gold and silver cyanide complexes in the zinc precipitation process. Gold and silver precipitation are improved by adding lead acetate or lead nitrate to the solution. The precipitation reaction for gold is:



The solution containing the precipitate is filtered and dried for smelting.

#### Cyanide in Spent Leach Piles

Very little data exists on the amounts and forms of cyanide in spent leach piles. It is difficult to compare the limited data that exists since researchers are not using a standardized method of sampling the spent ore heaps or leaching the solid sample before analysis. The cyanide content and forms in spent leach piles will depend on the ore mineralogy, ore pH, heap permeability, the thickness of the heap, cyanide concentration in process solution, solubility and dissociation rate of metal cyanide complexes, temperature, the type and application of rinsing solutions, and the rate of release of cyanide from the pile. Volatilization is probably the most important process for the removal of cyanide from spent ore heaps after the heaps have been rinsed. Atmospheric sampling data are not available for the low level release of HCN from spent leach piles.

Research is currently being conducted by J. Hendrix (University of Nevada, personal communication, 1986) on cyanide in spent leach piles. His research consists of 1) experimentation with a leaching column containing ore in the laboratory and 2) collection of samples (representative sampling on a grid) from spent leach piles. Dr. Hendrix is also developing analytical methods to determine the amounts of specific metal cyanide complexes present.

Engelhardt (1985) and Milligan (1985a) studied the decay of cyanide after the heap leaching of some tailings (15 percent plus-100 mesh) that were formerly processed for lead, zinc, and silver (sulfide and oxide circuit) in the 1940's and 1950's. The location of this operation was in a desert area. Approximately 5,400 kilograms (12,000 pounds) or 11.5 percent of the cyanide remained in the spent heaps, after rinsing the 76,000 metric tons (84,000 short tons) of ore. A time-series study was initiated to examine the natural dissipation of cyanide levels in the ore. Samples were collected from 11 areas on the heap by driving a 3.8 centimeters (1.5 inch) pipe through the heap to the pad. Samples were agitated for one hour with distilled water and the slurry was filtered to recover the solution. After adjusting the pH to 12.0, the samples were analyzed for free cyanide. Sampling was conducted in January (3 months after the leaching process ceased), March, June, and September, 1983 and 6 months later in March, 1984. The pH in the heaps fell from 10.5 at the cessation of the operation to approximately 9 in late 1984. Results showing substantial decreases in free cyanide concentrations between the initial and final sampling periods are presented in Table B-8. Total cyanide data was not reported but it is stated that total cyanide was almost the same as free cyanide implying that there are no significant amounts of complexes. The data showed little correlation of cyanide concentration with depth. Based on these data (relatively few data points), the authors stated that at the present rate of degradation, it would take approximately four years for the cyanide concentration of the spent heap pile to decay to 1 mg/kg.

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TABLE B-8

FREE CYANIDE CONCENTRATIONS IN ELEVEN  
LOCATIONS IN THE DARWIN HEAP

Darwin ID No.	Heap No.	Percent Moisture		Free Cyanide (mg/kg)		Percent Loss of Free Cyanide During 15 Months
		Jan 83	Mar 84	Jan 83	Jan 84	
Q3S2	1	14.6	14.6	102.6	<6.8	93.4
Q3S3	2	14.0	13.0	118.8	13.4	88.7
Q3S4	3	16.4	15.5	196.2	23.8	87.9
Q6S1	4	14.7	14.6	144.8	22.2	84.7
Q6S2	5	14.6	12.5	87.2	20.0	77.1
Q6S3	6	15.9	14.3	155.0	28.4	81.7
Q6S4	7	15.2	12.0	91.4	<6.8	92.6
Q9S1	8	14.3	12.2	146.8	37.5	74.5
Q9S2	9	14.8	11.9	34.7	<6.8	80.4
Q9S3	10	14.5	11.8	8.5	<6.8	21.2
Q9S4	11	13.4	11.4	7.7	<6.8	16.9

Source: Engelhardt, 1985; Milligan, 1985a.

Research on the destruction of cyanide in the leached heaps was conducted at the Stibnite Mine in Idaho (Stotts, 1985). After leaching was completed, a solution containing chlorine and lime was sprayed on the heaps. The effluent from the rinsing was recycled through the neutralization system until it contained a free cyanide concentration of 0.2 mg/l. After a 0.2 mg/l concentration was reached, hourly testing of the solution was done over a period of 24 hours. If the 24 hour average free cyanide concentration did not exceed 0.2 mg/l and no single sample exceeded 1.0 mg/l, then the heap was environmentally suitable for disposal as required by the operator's agreement with the U.S. Forest Service. If, however, the 24 hour test failed to meet these requirements, the entire procedure was repeated. An analysis for a sample from the chlorine pond (rinsing solution) is given in Table B-9. This table shows the metals associated with the ore at Stibnite, some of which may form salts of metal cyanide complexes and remain in the spent ore. After treatment with chlorine, the spent ore was hauled to an old tailings site and spread out in thin layered lifts of 0.3 to 0.6 meters (1 to 2 feet).

Ten locations in the spent ore were sampled at 15 to 30 centimeters (6 to 12 inches) below the surface at one, five, and ten day intervals. Cyanide was analyzed from the leachate produced from the mixing of 25 grams of ore placed in 50 milliliters of cyanide-free caustic soda (NaOH) solution at 20 percent strength. The ore was leached for 12 to 24 hours. Results of the time series decay of cyanide for eight of the samples are shown in Figure B-4. The average 10-day decrease was approximately 50 percent of the content on the first day, with a range from about 10 percent for the samples with a very low starting concentration to a high of nearly 80 percent for samples having a higher starting concentration.

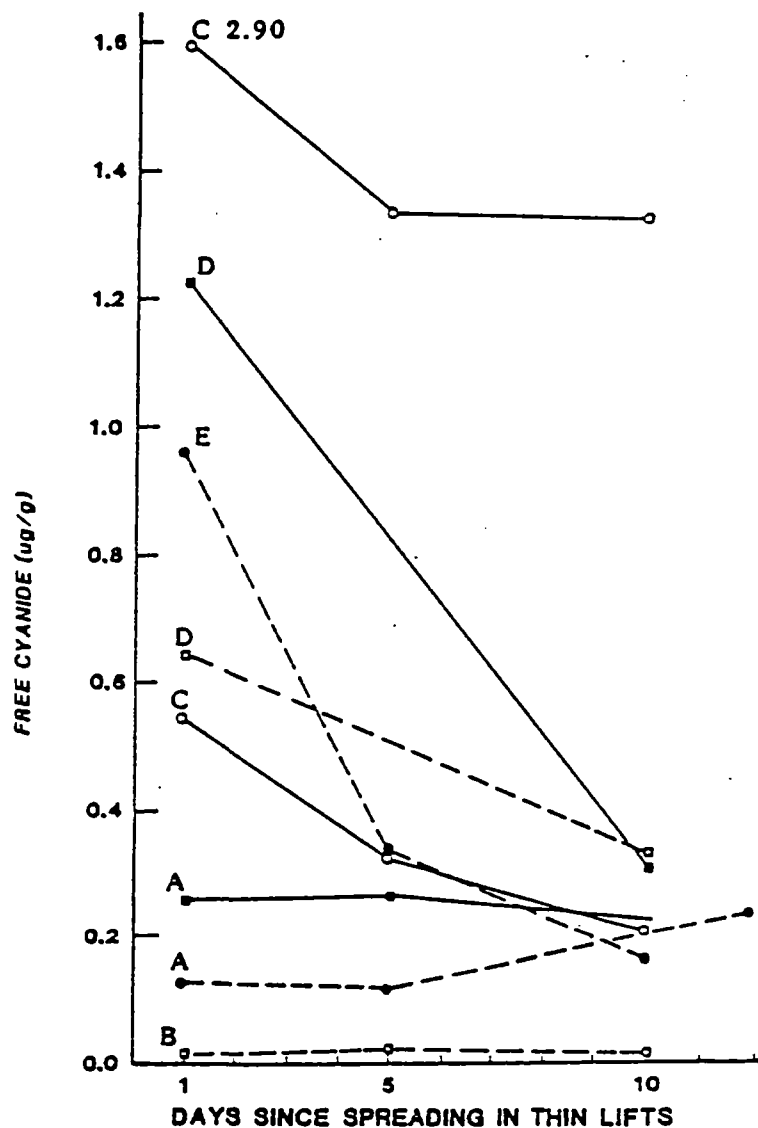
Ray (1985) sampled various heap leach piles in the southeastern desert of California and found that total cyanide levels were highly dependent upon the mineral composition of the ore (Table B-10). The sampling procedure was not described. The total cyanide analysis was conducted on a 20 gram sample that was subjected to a 24-hour leaching

TABLE B-9  
SOLUTION SAMPLE OF CHLORINE POND AT STIBNITE MINE, IDAHO  
August 24, 1983

Chloride	1,724 mg/l
Arsenic	0.271 mg/l
Antimony	0.021 mg/l
Calcium	560 mg/l
Copper	0.071 mg/l
Iron	0.590 mg/l
Lead	0.034 mg/l
Mercury	0.357 mg/l
Sodium	135 mg/l
Zinc	0.030 mg/l
Cadmium	0.016 mg/l

Source: Stotts, 1985.

**FIGURE B-4**  
**CYANIDE DEGRADATION IN TREATED WASTE**  
**ORE FROM STIBNITE MINE, IDAHO**



NOTE: THE LETTERS (A to E) REPRESENT LOCATIONS. TWO SAMPLES WERE TAKEN FROM SEVERAL LOCATIONS (A, C, AND D). THE SOLID AND DASHED LINES ARE FOR CLARITY.



TABLE B-10

TOTAL CYANIDE CONCENTRATIONS FOR VARIOUS  
HEAP LEACH OPERATIONS IN CALIFORNIA

<u>Description of Ore Samples</u>	<u>Run No.</u>	<u>mg/kg</u>
Samples low in iron	1	0.97
	2	0.41
	3	0.24
	4	0.42
	5	0.12
	6	0.27
	7	1.5
	8	0.90
Samples high in iron and copper	9	75
	10	34
	11	9.0
Samples high in iron, mined for silver	12	17.1
	13	5.9
	14	11.2
	15	105
Samples high in copper	16	41
	17	83
	18	91
	19	5.7
Samples low in cyanicides	20	0.82
	21	<0.05
	22	<0.05
	23	<0.05
	24	1.0
	25	0.07
	26	<0.05
	27	0.12
	28	0.20
	29	<0.05
	30	<0.05

Source: Ray, 1985.

in the dark using a 1.25 N NaOH solution, filtration, and analysis of the filtrate by the EPA (1979) distillation/destruction method, followed by colorimetric measurement.

The California Regional Water Quality Control Board, Colorado River Basin, Region 7 (1985) use to require a 1.0 mg/kg limit on the total cyanide found in abandoned heap leach piles. After reviewing the literature, specifically fish toxicity studies and cyanide environmental chemistry, they have changed the limit to 10 mg/kg. Their rationale is that because iron is the major metal atom available for complexation, iron cyanides are expected to be the only strong complexes formed. Other complexes are weaker and can be expected to degrade readily to cyanide ion. Therefore, the major species to consider in heap leach piles are iron cyanides and cyanide ion. Since iron cyanides are considered to be of low toxicity and have proven to be generally non-leachable, only cyanide ion content should be considered. A cyanide level of 0.02 mg/l was acceptable to the Regional Board and after multiplying by 100 (their usual practice when accounting for dilution in the environment), a level of 2.0 mg/l was obtained. The analysis of the sample is performed by leaching 1 part solid to 5 parts liquid; using this ratio and 2.0 mg/l, the acceptable limit for a solid is 10 mg/kg. Based on this rationale requirements from the Regional Board, the Mesquite Mine was required to rinse as follows when abandoning heap leach piles: 1) 90 percent of at least 10 samples shall contain less than 10 mg/l free cyanide and 2) none of the samples shall contain more than 20 mg/l free cyanide.

A sample collected from leached ore (with pH of 8.3) at the Zortman and Landusky heap in Montana had a concentration of 4.5 mg/kg for both total cyanide and cyanide amenable to chlorination (ERCO, 1984). The method of analysis was that prescribed by the EPA (1982). Concentrations of total cyanide and cyanide amenable to chlorination in the inactive heap leach material (with pH of 8.8) from the Pinson Mine in Nevada were both less than 2 mg/kg.

The sample extraction or leaching method prior to analysis may determine the content of cyanide in the sample. Spent heap leach wastes from Tombstone Silver Mines, Inc. (Arizona) were sampled and 75 grams of sample were leached with 150 milliliters of water and 0.1 gram of lime (CaO) for 1 hour (Pahlman, 1986). Most of the values were less than 0.1 mg/l with a range of less than detectable to 0.40 mg/l. An assay method from the U.S. Bureau of Mines, in which extraction was allowed for 12 hours on 40 gram of sample with 200 milliliters of water and 1 gram of sodium hydroxide, gave cyanide values that were 2 to 10 times greater than the previous method. The range of cyanide concentrations was less than 0.25 to 0.86 mg/kg with more than half the values below the detection limit of 0.25 mg/kg.

Sampling was conducted of the runoff from test heaps at the Annie Creek Mine (South Dakota) that were neutralized with hypochlorite followed by water (McGrew, 1985). After the first month (1982) there was more than a 10-fold decrease in both total cyanide and weak acid dissociable cyanide with decreases of 300 to 3.4 mg/l and 300 to 10 mg/l, respectively. Values continued to decrease with a range of 0.2 to 0.01 mg/l weak acid dissociable cyanide for sampling in December, 1983 to June, 1985. The test heaps were also sampled with depth up to 1.8 meters (6 feet). Of a total of 30 samples analyzed for total cyanide at 0.3 meter (1 foot) intervals, 21 samples were less than the detection limit of 0.5 mg/l, five analyses were between 0.5 and 0.6 mg/l, three between 0.6 and 0.7 mg/l, and one was higher than 0.7 mg/l. Of the 30 samples, for weak acid dissociable cyanide, 28 were below the detection limit of 0.5 mg/l and 2 were between 0.5 and 0.6 mg/l. Samples were also taken of the clay liner directly below the heaps. Cyanide did not penetrate below a depth of 10 centimeters (4 inches) based on 23 samples analyzed at 5-centimeter (2-inch) depth intervals. Of the 23 total cyanide concentrations, only 5 had detectable levels which ranged from 1.29 to 2.92 mg/l in the 0- to 5-centimeter (0- to 2-inch) and 5- to 10-centimeter (2- to 4-inch) clay samples. Weak acid dissociable cyanide was detected in only one sample at 0.83 ppm in a 5 to 10 centimeter (2- to 4-inch) interval.

There also is little information on the content and forms of cyanide in leachate from spent heap leach piles. As a part of the study by Engelhardt (1985) and Milligan (1985a) described above, the entrained solution in the heaps was also sampled for cyanide content. The moisture content in the first sampling (January, 1983) ranged from 13.5 to 16.4 percent and the final sampling (March, 1984) ranged from 11.4 to 15.5 percent. The average values for the two sampling periods were 340 mg/l and 106 mg/l free cyanide, respectively.

#### Degradation of Cyanide at Heap leach Operations

During the course of operation and at closure, cyanide in spent ore piles and process solutions must be rendered harmless. There has been very little published on the treatment of cyanides in spent ore piles, while extensive literature exists on the treatment processes for solutions containing cyanide.

#### Spent Leach Heap Piles

Upon closure of spent heaps operators are using several different methods to expedite the destruction of cyanide in the heaps. The requirements for neutralization vary by state (Table B-11). Generally, the rinsing procedure consists of either applying fresh water or an alkaline solution containing chlorine to the heap. The resulting effluent is recycled through the heap after the rinseate is treated with a method to destroy cyanide. This process is repeated until the cyanide concentration required in the effluent is obtained. Methods for neutralizing cyanide in water are described in detail below. Examples of the amounts of cyanide remaining in spent piles after rinsing were discussed above.

Natural degradation processes including volatilization, photo-decomposition, oxidation, adsorption, and biodegradation continue to reduce levels of cyanide in the spent heaps after rinsing. Examples of some rates of cyanide degradation in spent heaps were discussed above.

TABLE B-11

WESTERN STATE REGULATIONS OR GUIDELINES FOR NEUTRALIZATION  
OF SPENT HEAP LEACH PILES

<u>State</u>	<u>Required Cyanide Content of Rinseate</u>
Arizona	Require the operators to show evidence there is no free cyanide; no recommendations for rinsing process (J. McCutchan, Arizona State Mine Inspector, personal communication, 1986).
California	Guidelines vary between Regional Boards. Region 5 - 0.35 mg/l free cyanide (D. Heiman, California Regional Quality Control Board - Region 5, personal communication, 1986). Region 6 - 0.2 mg/l free cyanide or 10 mg/kg total cyanide (M. Watkins, California Regional Water Quality Control Board - Region 6, personal communication, 1986). Region 7 - 2.0 mg/l or 10 mg/kg free cyanide (California Regional Water Quality Control Board, 1985).
Colorado	Considering developing guidelines. Recommend 2 mg/l free cyanide; in sensitive areas recommend 0.75 mg/l. Recommend fresh water or hydrogen peroxide for rinsing method (A. Baldrige, Colorado Mined Land Reclamation Division, personal communication, 1986).
Idaho	Developing regulations (I. Nautch, Idaho Water Quality Bureau, personal communication, 1986). Requirements for Stibnite (0.2 mg/l free cyanide); recommend hypochlorite rinse.
Montana	Developing regulations/guidelines (D. Smith, Montana Department of State Lands, personal communication, 1986).
New Mexico	Guidelines; 45 kg (100 lb) sample rinsed can not have more than 100 mg/l total cyanide (A. Die, New Mexico Environmental Improvement Division, personal communication, 1986).
Nevada	Required to rinse with water until pH of rinse water is 8.5 for three consecutive days (H. Van Driaen, Nevada Division of Environmental Protection, personal communication, 1986).

(Continued)

TABLE B-11 (Continued)

<u>State</u>	<u>Required Cyanide Content of Rinseate</u>
Oregon	Guidelines of 0.01 mg/l total cyanide; recommend hypochlorite rinse (K. Ashbaker, Oregon Department of Environmental Quality, personal communication, 1986).
South Dakota	Guidelines for Wharf Resources (0.75 mg/l total cyanide); currently working on rinsing method recommendation (B. Townsend, South Dakota Department of Natural Resources, personal communication, 1986).
Utah	Guidelines for Mercur Mine (5 mg/l free cyanide); no recommendations for rinsing method (C. Dietz, Utah Water Pollution Control, personal communication, 1986).
Washington	Developing regulations/guidelines (B. Lingley, Washington Department of Natural Resources, personal communication, 1986).
Wyoming	No regulations or guidelines (C. Bosco, Wyoming Land Quality Division, personal communication, 1986).

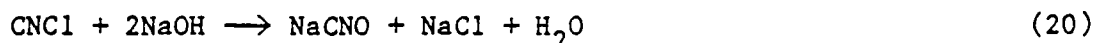
### Process Cyanide Solutions

Barren solution should be subject to cyanide destruction upon closure. In addition, during fall some barren solution may need to be treated and released (possibly as a land application) in anticipation of winter precipitation to meet water balance requirements. The rinsing solution used to neutralize the spent ore heaps will also require a treatment process. The methods described below are based on volatilization (natural degradation), oxidation (alkaline chlorination, hydrogen peroxide, Inco process), and biological processes. The major treatment processes that are used or may be used at leaching operations are summarized here; these and other processes are described in more detail in Huiatt et al. (1983) and Scott (1985).

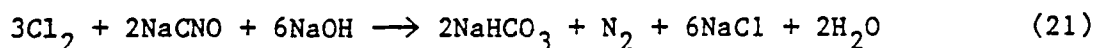
Natural Degradation. The results of studies of barren and tailings ponds in Canada (Simovic et al., 1985; Schmidt et al., 1981) show that natural degradation of cyanide occurs with over 90 percent of cyanide decrease attributed to volatilization of molecular HCN. For example, the cyanide content of a waste barren pond decreased from 64 mg/l in March to 0.05 mg/l in the following August and the pH dropped from 10.5 to 7.0 (Schmidt et al., 1981). The pH drop was a result of natural carbonation and the hydrolysis of thiocyanate. Some photodecomposition of ferrocyanides occurred.

A model has been developed to predict the natural degradation of cyanide in gold mill effluents, specifically barren solution and tailings pond water (Simovic et al., 1985; Simovic and Snodgrass, 1985). The model utilized the results from the synthetic solutions described in the section, Dissociation of Metal Cyanide Complex Ions, and assumed that the decay rate of a metal cyanide complex and subsequent volatilization of HCN control the disappearance of total cyanide from solution, with metal cyanide complex decay being the rate controlling factor. The model was used to predict degradation times for representative wastewater systems at two Canadian gold mills. The degradation of cyanide from tailings pond water was predicted very closely, but the model needs further calibration for the barren solutions.

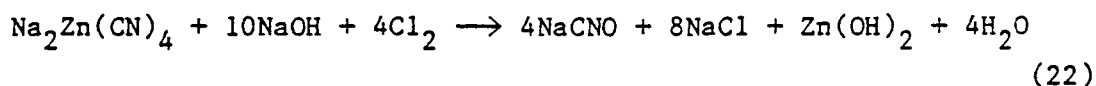
Alkaline Chlorination. The most developed of all the available methods in regards to background experience, operational simplicity, control techniques, availability of equipment, and engineering expertise, is alkaline chlorination (Ingles and Scott, 1981). The complete oxidation of cyanide to nitrogen and bicarbonate requires two stages (Scott, 1985). In the first stage cyanide undergoes oxidation and hydrolysis at a minimum pH of 10.5 as shown:



During the second stage of the process, cyanate is further oxidized to nitrogen and bicarbonate at a pH of about 8.5, which can be represented by the overall reaction:



Metal cyanide complexes are oxidized during the first stage of the process as shown for the zinc cyanide complex:



The alkaline chlorination method destroys free cyanide ion, hydrogen cyanide, and cyanide from most metal cyanide complexes with the exception of iron cyanide complexes. Table B-12 presents the advantages and disadvantages of alkaline chlorination.

Hydrogen Peroxide. The hydrogen peroxide method, which is well known and widely used in the treatment of effluents from the steel hardening and other industries, is now being applied to the gold mining industry. The hydrogen peroxide method is favorable from the environmental view since no toxic by-products are generated nor are additional chemicals added which may be detrimental to the environment (Knorre and Griffiths, 1985). In addition, metals are precipitated as hydroxides. The reaction for the oxidation of cyanide to cyanate is:





TABLE B-12

ADVANTAGES AND DISADVANTAGES OF ALKALINE CHLORINATION

ADVANTAGES OF ALKALINE CHLORINATION

- 1) Very widely-used method, expertise is available.
- 2) Influent to process already basic.
- 3) Reactions complete and reasonably rapid.
- 4) Toxic metals removed.
- 5) Chlorine readily available in several different forms.
- 6) Readily adaptable to either continuous or batch operation.
- 7) Capital outlay relatively low.
- 8) Good fail-safe control.
- 9) Easily controlled to first stage of oxidation, if disposal of  $\text{CNO}^-$  is permitted.

DISADVANTAGES OF ALKALINE CHLORINATION

- 1) Reagent costs are high, particularly if complete oxidation is required. Thiocyanate, thio-salts and ammonia are additional heavy consumers of chlorine.
- 2) Requires careful control of pH to prevent formation of cyanogen chloride which is very toxic.
- 3) Cyanide is not recovered.
- 4) Hexacyanoferrates are not usually decomposed.
- 5) Metal content is not recovered.
- 6) The chloride content of the effluent is increased in direct proportion to the amount of chlorine added.
- 7) There is a possibility of forming toxic chlorine derivatives (e.g. chlorinated organic compounds) which will require further treatment.
- 8) Residual excess chlorine can be toxic to aquatic species.<sup>a/</sup>

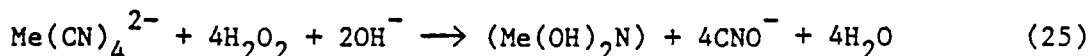
a/ Clean-up of excess chlorine is readily accomplished with  $\text{S}_2\text{O}_3^{2-}$  or  $\text{H}_2\text{O}_2$ , but an extra step is needed.

Source: Adapted from Ritcey and McNamara, .1978; cited by Ingles and Scott, 1981.

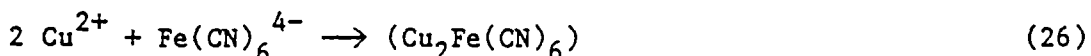
The cyanate formed in this reaction hydrolyzes further to form ammonium and carbonate ions:



The reaction for the precipitation of metals is:

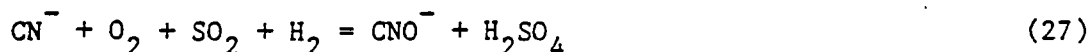


Complex iron cyanides are too stable to be oxidized but they may be precipitated by the addition of copper:



The hydrogen peroxide method destroys hydrogen cyanide, cyanide ion, and cyanide in copper, zinc, and nickel cyanide complexes. If copper is added, iron cyanide complexes may be precipitated.

Inco Process. This method was originally developed for base metal mining operations, but is now used by a number of gold mines in Canada. Oxidation by  $\text{SO}_2$  in air in the presence of a copper catalyst causes the rapid removal of cyanide and metal cyanide complexes. The overall reaction is the oxidation of cyanide to cyanate which is described by the equation:



Iron cyanide complexes are removed by precipitation as copper or zinc ferrocyanides. The metals except for iron are precipitated as metal hydroxides. Thiocyanate is not removed.

Biological Treatment. Homestake Mining Company has recently developed a biological treatment method for removing cyanide and metal ions from effluents (Mudder and Whitlock, 1983). An essential requirement for successful operation of this process is the ability to blend mine water at 21 to 29° C (70 to 85° F) with tailings impoundment water at 1.1 to 21° C (34 to 70° F) to maintain a year round combined wastewater temperature sufficiently warm at 10 to 18° C (50 to 65° F) to sustain effective biological process rates. The two stages of the the methods are 1) bacterial oxidation of cyanide and thiocyanate to carbon dioxide, sulfate, and ammonia concurrent with the adsorption of metals

by the bacteria and 2) bacterial nitrification of ammonia to nitrate. The only reagents added are soda ash as an inorganic carbon source to aid nitrification, and phosphorus as a trace nutrient. Total cyanide is reduced to 0.30 mg/l from an influent concentration of 2.0 mg/l; thiocyanate content is reduced to less than 0.10 mg/l from 50.0 mg/l. Metals are returned to the tailings pond.

#### Environmental Fate of Cyanide in Heap Leach Mining Wastes

The chemical and biological processes controlling the fate of cyanide in heap leach mining operations are summarized in Figure 20 (Chapter 4). These processes were discussed in detail in the section entitled, Environmental Fate of Cyanide. Heap leach mining wastes may contain free cyanide ( $\text{HCN}$  and  $\text{CN}^-$ ), metal cyanide complexes, and salts of metal cyanide complexes. The process controlling the fate of free cyanide in these wastes is volatilization of  $\text{HCN}$  to the atmosphere.  $\text{HCN}$  will diffuse upward through the troposphere and is destroyed in the stratosphere (Singh et al., 1984). An important control on volatilization is pH; below a pH of 9,  $\text{HCN}$  is predominant over cyanide ion.

Metal cyanide complexes such as iron, copper, zinc, nickel, cobalt, and cadmium, which are the most common at gold and silver operations (Huiatt, 1985), decompose and release cyanide ion at varying rates. Zinc and cadmium complexes, the least stable complexes, readily decompose as free cyanide decreases during the rinsing process. Strong complexes such as iron cyanide complex may remain in the ore. Iron cyanide complexes have been found to degrade in solutions exposed to ultraviolet light, but the photochemical effect on the solid species is unknown. As the concentration of free cyanide decreases below the concentration of metal cyanide complexes, the slower rate of decomposition of metal cyanide complexes becomes the rate controlling step for the volatilization of free cyanide. Other compounds that may be very sparingly soluble in water are iron, nickel, cobalt, and copper salts of iron complex cyanide ions. Until the presence of these complexes and compounds is exhausted, very small amounts of free cyanide may be released in the spent heap pile.

Besides volatilization directly from the mining wastes, a secondary transport process is the leaching of cyanide and any soluble metal cyanide complexes from the mining wastes and their transport into the environment if uncontained. Also possible would be the accidental release of cyanide process solution through pond overflows and pad or pond leaks (refer to Appendix D for reported accidents at heap leach mining operations). Volatilization is an important process for removing cyanide from surface water whereas other processes (biodegradation, reaction of cyanide to ammonia and formate, sorption, complexation, and others) may be more important for soil and ground water. The discussion of the mobility of cyanide in surface water, ground water, and soils is contained in the final part of the section, Environmental Fate of Cyanide.

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